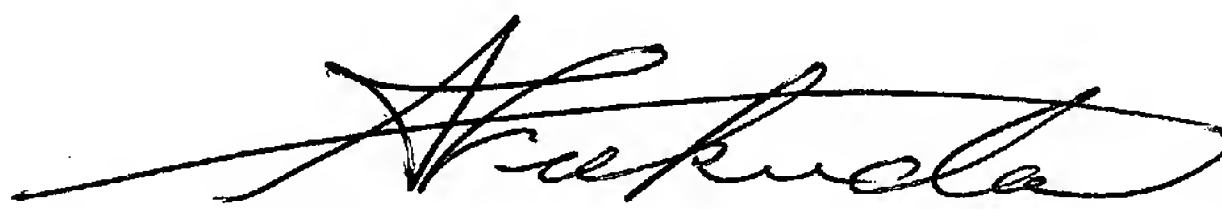


STATEMENT

I, Akihito FUKUDA—of Toranomom East Bldg. 7-13,
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Japan—hereby declare that I am conversant in both Japanese
and English and that I believe the following is a true and correct
translation of a certified copy of Japanese Patent Application No.
2003-363728.

Date: January 14, 2010

A handwritten signature in black ink, appearing to read 'Akihito FUKUDA', written over a horizontal line.

Akihito FUKUDA

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[List of Documents Attached]

[Name of Document]	Claims	1
[Name of Document]	Specification	1
[Name of Document]	Abstract	1

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[Designation of Document] CLAIMS

[Claim 1]

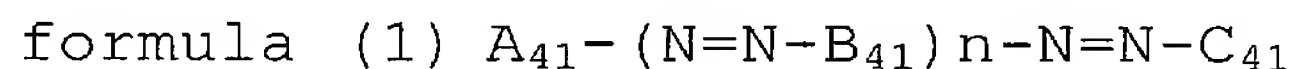
A black ink for inkjet, which comprises at least two dyes each having a value of λ_{\max} within a range of from 500 nm to 700 nm, and having a half-value width of at least 100 nm in the absorption spectrum of the diluted solution thereof standardized to have an absorbance of 1.0, both dissolved or dispersed in an aqueous medium, and in which at least one dye has a positive oxidation potential over 1.0 V (vs SCE).

[Claim 2]

The black ink for inkjet as claimed in claim 1, which further contains at least one dye having a value of λ_{\max} within a range of from 350 nm to 500 nm.

[Claim 3]

The black ink for inkjet as claimed in claim 1 or 2, wherein at least one dye is a compound represented by the following formula (1):



wherein A_{41} , B_{41} and C_{41} each independently represent an aromatic group or a heterocyclic group that may be further substituted; n is an integer of 0 or more.

[Claim 4]

The black ink for inkjet as claimed in any of claims 1 to 3, wherein at least one dye is a compound represented by the following formula (2):

formula (2) $P-(N=N-Qx)_y-N=N-R$

wherein P, Q and R each represent an optionally-substituted aromatic group; x is an integer of 1 or more; and y is an integer of 0 or more.

[Claim 5]

The black ink for inkjet as claimed in claim 4, wherein Q in formula (2) is a naphthalene-bicyclic or more polycyclic aromatic ring, and x is an integer of 1 or more.

[Claim 6]

The black ink for inkjet as claimed in any of claims 1 to 5, wherein the dye having a value of λ_{max} within a range of from 350 nm to 500 nm is a compound represented by formula (1).

[Claim 7]

An ink set for inkjet comprising at least one black ink as claimed in any of claims 1 to 6.

[Designation of Document] SPECIFICATION

[Title of the Invention] INK AND INK SET FOR INKJET

[Technical Field]

[0001]

The present invention relates to a black ink and ink set for inkjet which is attained high-density black images, and good image durability and ink jet out stability.

[Background Art]

[0002]

With the recent popularization of computers, inkjet printers are much used for printing on paper, films, cloths and others, not only in office work but also for home use.

The inkjet recoding method includes a system of applying pressure to ink drops by the use of a piezoelectric device to thereby make the ink drops jet out, a system of thermally bubbling ink to jet the ink drops, a system of using ultrasonic waves, and a system of sucking and jetting ink drops by electrostatic force. For the ink compositions for such inkjet recording, usable are aqueous inks, oily inks and solid (hot-melt) inks. Of those, aqueous inks are most used because of their productivity, handlability, odorlessness and safety.

[0003]

Colorant to be used in such inkjet recording inks must satisfy the following requirements: Its solubility in solvent is good; it enables high-density recording; its hue is good; it is fast to light, heat, air, water and chemicals; it well fixes in image-receiving material and hardly bleeds out; its storage stability in inks is good; it is not toxic; its purity is high; and it is inexpensive and is readily available. However, it is extremely difficult to seek such colorant that satisfies all these requirements on a high level.

Various dyes and pigments have been already proposed for inkjet, and are now in practical use. At present, however, no one knows colorant that satisfies all the requirements. Dyes and pigments heretofore well known in the art such as those listed in Color Index (C.I.) could hardly satisfy both the color hue and the fastness, which inks for inkjet need.

[0004]

The present inventors have studied an ink for inkjet that contain dyes. However, we have further known that aqueous black inks are problematic in that their image durability is low. Apart from carbon black, there are known few black dyes capable of providing high-quality black images such as letters by themselves, and we have known that some different types of dyes each having a

different absorption spectrum must be mixed for forming the intended black images. In this case, however, we have further known that the fading rate may differ between the dyes mixed, and that, when the dyes having a broad absorption characteristic have faded and changed in their absorption wavelength, then the quality of the black-containing image is significantly worsened.

To evade the problem, a method of mixing different types of dyes may be taken into consideration. However, when dyes in a group having the same structure are mixed, then it causes a problem in that a black image having a high reflection density is difficult to obtain.

On the other hand, water-soluble black inks must satisfy the absorption characteristics of covering a broad wavelength range, and are therefore problematic in that their solid concentration is apt to increase and they may worsen the jet-out stability of inks.

[Disclosure of the Invention]

[Problem that the Invention is to Solve]

[0005]

An object of the invention is to provide a black ink and ink set for inkjet which includes high-density black images, and good image durability and ink jet out stability.

[Means for Solving the Problem]

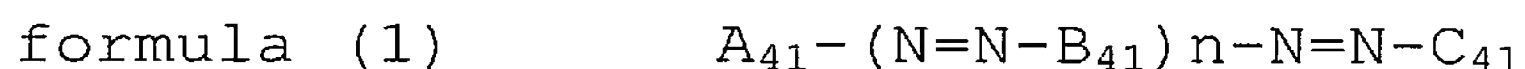
[0006]

The object of the invention is attained by inks and ink sets for inkjet of the following items 1 to 7.

1. A black ink for inkjet, which comprises at least two dyes each having a value of λ_{\max} within a range of from 500 nm to 700 nm, and having a half-value width of at least 100 nm in the absorption spectrum of the diluted solution thereof standardized to have an absorbance of 1.0, both dissolved or dispersed in an aqueous medium, and in which at least one dye has a positive oxidation potential over 1.0 V (vs SCE).

2. The black ink for inkjet of above 1, which further contains at least one dye having a value of λ_{\max} within a range of from 350 nm to 500 nm.

3. The black ink for inkjet of above 1 or 2, wherein at least one dye is a compound represented by the following formula (1):



wherein A_{41} , B_{41} and C_{41} each independently represent an aromatic group or a heterocyclic group that may be further substituted; n is an integer of 0 or more.

4. The black ink for inkjet of any of above 1 to 3, wherein at least one dye is a compound represented by the following formula (2):



wherein P, Q and R each represent an optionally-substituted aromatic group; x is an integer of 1 or more; and y is an integer of 0 or more.

5. The black ink for inkjet of above 4, wherein Q in formula (2) is a naphthalene-bicyclic or more polycyclic aromatic ring, and x is an integer of 1 or more.

6. The black ink for inkjet of any of above 1 to 5, wherein the dye having a value of λ_{max} within a range of from 350 nm to 500 nm is a compound represented by formula (1).

7. An ink set for inkjet including at least one black ink of in any of 1 to 6

[0007]

Using two or more different types of black dyes in combination, the invention has attained black inks having good absorption characteristics and having a flat spectrum. Accordingly, the invention has attained high-density black images, and has solved the problem with black inks that has heretofore been discussed in the related art in point of increasing their solubility.

[Advantage of the Invention]

[0008]

The black inks and ink sets of the invention have good ink-jet stability and provide high-density images of

good durability.

[Best Mode for Carrying out the Invention]

[0009]

The invention is described in detail hereinunder.

Preferably, the black ink of the invention contains at least two dyes (L) each having a value of λ_{\max} within a range of from 500 nm to 700 nm, and having a half-value width ($W\lambda_{1/2}$) of at least 100 nm (preferably from 120 nm to 500 nm, more preferably from 120 nm to 350 nm) in the absorption spectrum of the diluted solution thereof standardized to have an absorbance of 1.0.

[0010]

Preferably, at least one of the dyes (L) for use in the black ink has a positive oxidation potential over 1.0 V (vs SCE), more preferably over 1.1 V (vs SCE), even more preferably over 1.2 V (vs SCE), most preferably over 1.25 V (vs SCE).

[0011]

The oxidation potential (E_{ox}) of dyes may be readily measured by anyone skilled in the art. For measuring it, herein employable are various methods of, for example, dropping-mercury electrode method (polarography), cyclic voltammetry (CV) in an aqueous solution or a water-mixed solvent system with a dye dissolved therein, rotary ring-disc electrode method or combed electrode method.

[0012]

The method for the measurement is described in, for example, P. Delahay, *New Instrumental Methods in Electrochemistry*, 1954, Interscience Publishers; A. J. Bard et al., *Electrochemical Methods*, 1980, John Wiley & Sons; A. Fujishima et al., *Electrochemical Measurement Methods*, 1984, Gihodo Publishing.

[0013]

Concretely, the oxidation potential may be measured as follows: A sample to be analyzed is dissolved in a solvent such as dimethylformamide or acetonitrile that contains a supporting electrolyte such as sodium perchlorate or tetrapropylammonium perchlorate to have a concentration of from 1×10^{-4} to 1×10^{-6} mol/liter, and its value of oxidation potential versus SCE (saturated calomel electrode) is measured through cyclic voltammetry or direct current polarography. The value of oxidation potential may deviate by tens millivolts or so, owing to the influence of the liquid junction potential or the sample solution resistance thereon, but it may be calibrated with a standard sample (e.g., hydroquinone). In that manner, the reproducibility of the thus-measured potential value is ensured. In the invention, the oxidation potential of dye is measured in dimethylformamide (in this, the concentration of the dye is $0.001 \text{ mol} \cdot \text{dm}^{-3}$) that

contains $0.1 \text{ mol} \cdot \text{dm}^{-3}$ of a supporting electrolyte, tetrapropylammonium perchlorate (vs SCE), in order to indiscriminately define the potential by direct current polarography. In case that water soluble dyes is difficult to directly solve in N,N-dimethyl formamide, the oxidation potential is measured by solving dyes with little water as possible, following diluting with N,N-dimethyl formamide to be 2% or less of water content.

[0014]

Eox indicates the electron mobility from sample to electrode. Samples having a larger value of Eox (those having a positive oxidation potential) mean that electrons move more hardly from them to electrode, or that is, the samples are more hardly oxidized. Relative to the structure of compounds, introduction of an electron-attractive group makes the compounds have a positive oxidation potential while introduction of an electron-donating group makes them have a negative oxidation potential. In the invention, it is desirable that an electron-attractive group is introduced into the skeleton of the dyes to thereby make the dyes have a positive oxidation potential, in order to lower the reactivity of the dyes with ozone, a type of electrophilic agent.

[0015]

In the invention, the dyes (L) are mixed and dissolved or dispersed in an aqueous medium to prepare a black ink. Preferably, the black ink contains the dyes mentioned below.

[0016]

The dye (L) may be used alone for black ink, so far as it may realize a "tight" black image of high quality (in which none of B, G and R color tones are highlighted irrespective of the viewing light source) by itself. In general, however, the dye is combined with any other dye capable of covering the region that is poorly absorbed by the dye (L). Concretely, it is desirable that the dye (L) is combined with a dye (S) having a main absorption in a yellow region on the short wavelength side (and having λ_{\max} of from 350 to 500 nm). As the case may be, the dye (L) may also be combined with any other dye to form black ink.

[0017]

Preferably, the black ink of the invention contains the azo dye of formula (1). The azo dye of formula (1) includes the dye (L) having a value of λ_{\max} within a range of from 500 nm to 700 nm, and having a half-value width of at least 100 nm in the absorption spectrum of the diluted solution thereof standardized to have an absorbance of 1.0. Apart from it, the azo dye of formula

(1) further includes the dye (S) having a value of λ_{\max} within a range of from 350 nm to 500 nm. Preferably, at least one dyes (L) in the black ink of the invention is the dye of formula (1), more preferably, both at least one dye (L) and at least one dye (S) are the dye of formula (1). Even more preferably, the dye of formula (1) accounts for at least 50 % by mass of all the dyes in the ink.

[0018]

Preferably, the black ink of the invention contains an additional azo dye of formula (2) in addition to the dye mentioned above. Preferably, the dye of formula (2) corresponds to the dye (L) having a value of λ_{\max} within a range of from 500 nm to 700 nm, and having a half-value width of at least 100 nm in the absorption spectrum of the diluted solution thereof standardized to have an absorbance of 1.0. Like the dye of formula (1), the dye of formula (2) may also be the dye (S) having a value of λ_{\max} within a range of from 350 nm to 500 nm.

The dye of formula (2) is a dye classified in a group of aromatic bisazo dyes, and different from the dye of formula (1), this is a compound in which the chromophoric site is entirely formed of hydrocarbon rings. Examples of the dye are described in Japanese Patents 3,428,178 and 2,428,263, and in CN136830-A.

[0019]

Of the dyes represented by formulae (1) and (2), those having a high oxidation potential and having a high degree of associability are especially preferred for use in the invention. For the purpose, it is desirable that the dyes are so designed that a larger number of electron-attractive groups could be in the molecule and the π -electron density existing in the main aromatic rings could be lowered, or are so designed that the molecule could have a plain structure capable of promoting association and could have multiple, strongly-interactive groups as the intermolecular substituents therein so as to induce molecular association.

[0020]

The strongly-interactive groups are, for example, hydrogen-bonding groups, and they are preferably -COOH, -OH, -SO₂NH-, -CONH- group, more preferably having -CONH-group. It is desirable that the dye molecule has a plurality of such hydrogen-bonding groups therein. Also preferably, the dye molecule has a number of plain-structured groups via which the molecules could readily overlap with each other. The groups are, for example, a biphenyl group and a naphthyl group.

[0021]

Regarding the dyes of high associability, when the

spectrum of the dye is measured as an aqueous solution thereof having a concentration of 0.025 mmol/liter, in a cell having a light guide length of 1 cm, and when the spectrum of the dye is measured as an aqueous solution thereof having a concentration of 50 mmol/liter in a cell having a light guide length of 5 μ m, then the position of λ_{max} in the spectra and the absorbance differ from each other. In particular, the absorbance drastically changes. In general, when the absorbance of the high-concentration solution is divided by that of the low-concentration solution, then it preferably gives at least 1.0, more preferably at least 1.2, even more preferably at least 1.3.

[0022]

In the invention, the black ink is prepared by mixing the black dyes and dissolving or dispersing the resulting mixture in an aqueous medium. The preferred properties of the black ink for ink jet recording are that 1) its weather resistance is good and/or 2) the image does not lose the black balance even after faded. In order that the black ink of the invention could have the preferred properties, it is desirable that the black ink satisfies the following conditions.

[0023]

Using the black ink of the invention, 48-point size,

black square symbols of JIS code 2223 are printed, and their reflection density (D_{vis}) is measured via a status A filter (visual filter). This is an initial density of the sample. One example of the reflection densitometer equipped with a status A filter is an X-Rite densitometer. To measure the density of "black" herein, the measured data D_{vis} are referred to as the standard observation reflection density. The printed matter is forcedly faded by the use of an ozone fading tester where 5 ppm ozone is generated all the time. The period of time (t) in which the reflection density (D_{vis}) of the faded sample is reduced to 80 % of the initial density of the original sample is counted, and a forced fading rate constant (k_{vis}) is derived from a relational formula, $0.8 = \exp(-k_{vis} \cdot t)$.

Preferably, the rate constant (k_{vis}) of the black ink in the invention is at most 5.0×10^{-2} [hour⁻¹], more preferably at most 3.0×10^{-2} [hour⁻¹], even more preferably at most 1.0×10^{-2} [hour⁻¹].

[0024]

Using the black ink of the invention, 48-point size, black square symbols of JIS code 2223 are printed, and the reflection density of three colors C (cyan), M (magenta) and Y (yellow), except D_{vis} , is measured via a status A filter. Thus measured, the data are initial

density D_R , D_G and D_B . These data D_R , D_G and D_B indicate the C reflection density through red filter, the M reflection density through green filter, and the Y reflection density through blue filter, respectively. The printed matter is forcedly faded by the use of an ozone fading tester where 5 ppm ozone is generated all the time, in the same manner as above. From the period of time in which the reflection density D_R , D_G and D_B of the faded sample is reduced to 80 % of the initial density of the original sample, the forced fading rate constant (k_R , k_G , k_B) is derived in the same manner as above. When the ratio (R) of the maximum value to the minimum value of the three rate constants (for example, when k_R is the maximum value and the k_G is the minimum value, $R = k_R/k_G$) is calculated, the ratio (R) is preferably at most 1.2, more preferably at most 1.1, even more preferably at most 1.05.

[0025]

In the "printed matter with 48-point size, black square symbols of JIS code 2223 thereon" used in the above, the image is printed to a size that fully covers the aperture of the tester in order that it may be enough for the density measurement.

[0026]

Preferably, the ink for the ink set of the invention

is characterized by the following:

Concretely, at least two inks are used, and 15-stage gradation print samples are formed to a degree of at most up to 30 ml/m². The maximum value of the reflection density of the pattern (this is a value of density measured at a site where the reflection density is saturated and could no more increase even when the printing ink amount is increased) is higher on the side of the high-concentration ink.

[0027]

The ink set of the invention satisfies any one or more of these conditions. Preferably, it satisfies all these conditions.

[0028]

The dyes of formula (1) are described below.
wherein A₄₁, B₄₁ and C₄₁ each independently represent an aromatic group that may be further substituted (A₄₁ and C₄₁ are monovalent aromatic groups, for example an aryl group, and B₄₁ is a divalent aromatic group, for example an arylene group) or a heterocyclic group that may be further substituted (A₄₁ and C₄₁ are monovalent heterocyclic groups, and B₄₁ is a divalent heterocyclic group). n is an integer of 0 or more.

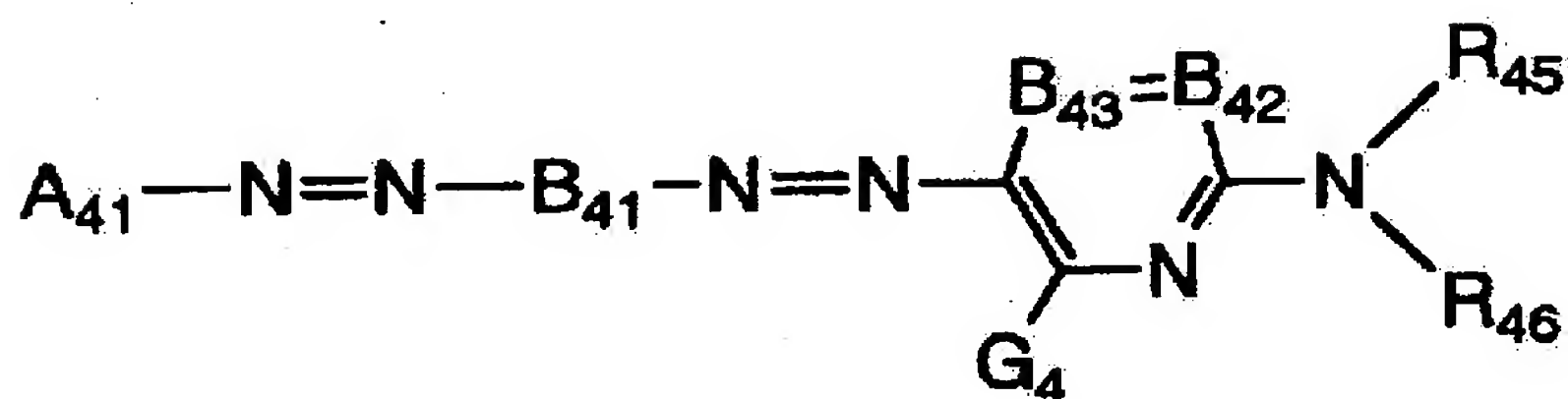
A substituent may be an arylazo group, or a heterocyclic azo group.

The azo dyes of formula (1) are more preferably those represented by the following formula (1-A):

[0029]

formula (1-A)

[chem.1]



[0030]

In formula (1-A), A_{41} and B_{41} are the same as A_{41} and B_{41} represented in formula (1). B_{42} and B_{43} each represent $=CR_{41}-$ or $-CR_{42}=$, or any one of them is a nitrogen atom and the other is $=CR_{41}-$ or $-CR_{42}=$.

[0031]

G_4 , R_{41} and R_{42} each independently represent a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic-oxycarbonyl group, an acyl group, a hydroxyl group, an alkoxy group, an aryloxy group, a heterocyclic-oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including alkylamino group, arylamino

group, heterocyclic-amino group), an acylamino group, an ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkyl or arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkyl or arylthio group, a heterocyclic-thio group, an alkyl or arylsulfonyl group, a heterocyclic sulfonyl group, an alkyl or arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group, or a sulfo group. These groups may be substituted.

[0032]

R_{45} and R_{46} each independently represent a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkyl or arylsulfonyl group, or a sulfamoyl group. These groups may be further substituted. R_{45} and R_{46} must not be hydrogen atoms at the same time.

R_{41} and R_{45} , or R_{45} and R_{46} may bond to each other to form a 5- or 6-membered ring..

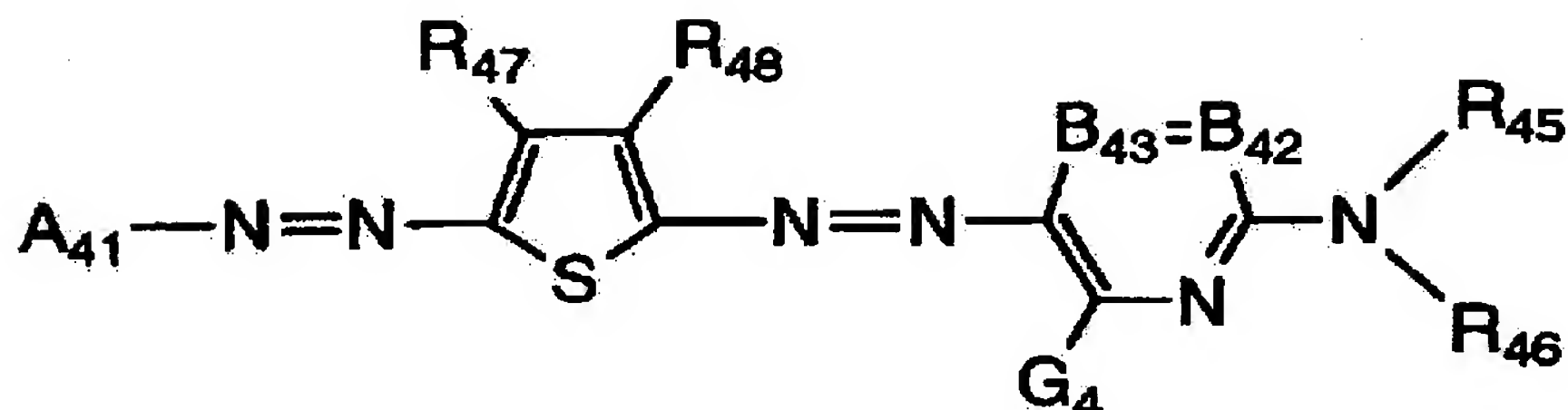
[0033]

The azo dyes represented by formula (1-A), are preferably those represented by the following formula (1-B):

[0034]

formula (1-B)

[chem.2]



[0035]

In formula (1-B), R_{47} and R_{48} have the same meaning as that of R_{41} in formula (1-A). A_{41} , R_{45} , R_{46} , B_{41} , B_{42} and G_4 have the same meanings as in formula (1-A).

[0036]

The terms (substituents) used in describing formula (1) and its more specific concepts, formulae (1-A) and (1-B) are described below. These are common to the description of formulae (1-C) and (1-D) given hereinunder.

[0037]

The halogen atom includes fluorine, chlorine and bromine atoms.

[0038]

The aliphatic group means to include an alkyl group, a substituted alkyl group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an aralkyl group and a substituted aralkyl group. The aliphatic group may be branched or may be cyclic. Preferably, the aliphatic

group has from 1 to 20 carbon atoms, more preferably from 1 to 16 carbon atoms. The aryl moiety of the aralkyl group and the substituted aralkyl group is preferably a phenyl or naphthyl group, more preferably a phenyl group. Examples of the aliphatic group are methyl, ethyl, butyl, isopropyl, t-butyl, hydroxyethyl, methoxyethyl, cyanoethyl, trifluoromethyl, 3-sulfopropyl, 4-sulfobutyl, cyclohexyl, benzyl, 2-phenethyl, vinyl and allyl groups.

[0039]

The monovalent aromatic group means to include an aryl group and a substituted aryl group. The aryl group is preferably a phenyl or naphthyl group, more preferably a phenyl group. The monovalent aromatic group preferably has from 6 to 20 carbon atoms, more preferably from 6 to 16 carbon atoms. Examples of the monovalent aromatic group are phenyl, p-tolyl, p-methoxyphenyl, o-chlorophenyl and m-(3-sulfopropylamino)phenyl groups. The divalent aromatic group corresponds to but differs from the monovalent aromatic group in that it is a divalent group. Its examples are phenylene, p-tolylene, p-methoxyphenylene, o-chlorophenylene, m-(3-sulfopropylamino)phenylene and naphthylene groups.

[0040]

The heterocyclic group means to include a substituted heterocyclic group and an unsubstituted

heterocyclic group. The hetero ring may be condensed with an aliphatic ring, an aromatic or any other hetero ring. The heterocyclic group is preferably a 5- or 6-membered heterocyclic group. The hetero atom to form the hetero ring includes N, O and S. Examples of the substituent of the substituted heterocyclic group are an aliphatic group, a halogen atom, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfamoyl group, a carbamoyl group, and an ionic hydrophilic group. Examples of hetero ring used in the monovalent heterocyclic group and the divalent heterocyclic group are pyridyl, thienyl, thiazolyl, benzothiazolyl, benzoxazolyl and furane ring.

[0041]

The carbamoyl group means to include a substituted carbamoyl group and an unsubstituted carbamoyl group. One example of the substituent is an alkyl group. Examples of the carbamoyl group are methylcarbamoyl and dimethylcarbamoyl groups.

[0042]

The alkoxycarbonyl group means to include a substituted alkoxycarbonyl group and an unsubstituted alkoxycarbonyl group. The alkoxycarbonyl group preferably has from 2 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. Examples

of the alkoxycarbonyl group are methoxycarbonyl and ethoxycarbonyl groups.

[0043]

The aryloxycarbonyl group means to include a substituted aryloxycarbonyl group and an unsubstituted aryloxycarbonyl group. The aryloxycarbonyl group preferably has from 7 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. One example of the alkoxycarbonyl group is a phenoxycarbonyl group.

[0044]

The heterocyclic-oxycarbonyl group means to include a substituted heterocyclic-oxycarbonyl group and an unsubstituted heterocyclic-oxycarbonyl group. The heterocyclic-oxycarbonyl group preferably has from 2 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. One example of the heterocyclic-oxycarbonyl group is a 2-pyridyloxycarbonyl group.

The acyl group means to include a substituted acyl group and an unsubstituted acyl group. The acyl group preferably has from 1 to 20 carbon atoms. One example of the substituent of is an ionic hydrophilic group. Examples of the acyl group are acetyl and benzoyl groups.

[0045]

The alkoxy group means to include a substituted alkoxy group and an unsubstituted alkoxy group. The alkoxy group preferably has from 1 to 20 carbon atoms. Examples of the substituent are an alkoxy group, a hydroxyl group, and a ionic hydrophilic group. Examples of the alkoxy group are methoxy, ethoxy, isopropoxy, methoxyethoxy, hydroxyethoxy and 3-carboxypropoxy groups.

[0046]

The aryloxy group means to include a substituted aryloxy group and an unsubstituted aryloxy group. The aryloxy group preferably has from 6 to 20 carbon atoms. Examples of the substituent are an alkoxy group and an ionic hydrophilic group. Examples of the aryloxy group are phenoxy, p-methoxyphenoxy and o-methoxyphenoxy groups.

[0047]

The heterocyclic-oxy group means to include a substituted heterocyclic-oxy group and an unsubstituted heterocyclic-oxy group. The heterocyclic-oxy group preferably has from 2 to 20 carbon atoms. Examples of the substituent are an alkyl group, an alkoxy group, and an ionic hydrophilic group. Examples of the heterocyclic-oxy group are 3-pyridyloxy and 3-thienyloxy groups.

[0048]

The silyloxy group is preferably substituted with an

aliphatic and/or aromatic group having from 1 to 20 carbon atoms. Examples of the silyloxy group are trimethylsilyloxy and diphenylmethyilsilyloxy groups.

[0049]

The acyloxy group means to include a substituted acyloxy group and an unsubstituted acyloxy group. The acyloxy group preferably has from 1 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. Examples of the acyloxy group are acetoxy and benzoyloxy groups.

[0050]

The carbamoyloxy group means to include a substituted carbamoyloxy group and an unsubstituted carbamoyloxy group. One example of the substituent is an alkyl group. One example of the carbamoyloxy group is an N-methylcarbamoyloxy group.

[0051]

The alkoxycarbonyloxy group means to include a substituted alkoxycarbonyloxy group and an unsubstituted alkoxycarbonyloxy group. The alkoxycarbonyloxy group preferably has from 2 to 20 carbon atoms. Examples of the alkoxycarbonyloxy group are methoxycarbonyloxy and isopropoxycarbonyloxy groups.

[0052]

The aryloxycarbonyloxy group means to include a

substituted aryloxy-carbonyloxy group and an unsubstituted aryloxy-carbonyloxy group. The aryloxy-carbonyloxy group preferably has from 7 to 20 carbon atoms. One example of the aryloxy-carbonyloxy group is a phenoxy-carbonyloxy group.

[0053]

The amino group means to include an amino group substituted with any of an alkyl group, an aryl group or a heterocyclic group. An alkyl group, an aryl group and a heterocyclic group may be further substituted. The alkylamino group preferably has from 1 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. Examples of the alkylamino group are methylamino and diethylamino groups.

The arylamino group means to include a substituted arylamino group and an unsubstituted arylamino group. The arylamino group preferably has from 6 to 20 carbon atoms. Examples of the substituent are a halogen atom and an ionic hydrophilic group. Examples of the arylamino group are anilino and 2-chlorophenylamino groups.

The heterocyclic amino group means to include a substituted heterocyclic amino group and an unsubstituted heterocyclic amino group. The heterocyclic amino group preferably has from 2 to 20 carbon atoms. Examples of

the substituent are an alkyl group, a halogen atom and an ionic hydrophilic group.

[0054]

The acylamino group means to include a substituted acylamino group and an unsubstituted acylamino group. The acylamino group preferably has from 2 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. Examples of the acylamino group are acetylamino, propionylamino, benzoylamino, N-phenylacetylamino and 3,5-disulfobenzoylamino groups.

[0055]

The ureido group means to include a substituted ureido group and an unsubstituted ureido group. The ureido group preferably has from 1 to 20 carbon atoms. Examples of the substituent are an alkyl group and an aryl group. Examples of the ureido group are 3-methylureido, 3,3-dimethylureido and 3-phenylureido groups.

[0056]

The sulfamoylamino group means to include a substituted sulfamoylamino group and an unsubstituted sulfamoylamino group. One example of the substituent is an alkyl group. One example of the sulfamoylamino group is an N,N-dipropylsulfamoylamino group.

[0057]

The alkoxycarbonylamino group means to include a substituted alkoxycarbonylamino group and an unsubstituted alkoxycarbonylamino group. The alkoxycarbonylamino group preferably has from 2 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. One example of the alkoxycarbonylamino group is an ethoxycarbonylamino group.

[0058]

The aryloxycarbonylamino group means to include a substituted aryloxycarbonylamino group and an unsubstituted aryloxycarbonylamino group. The aryloxycarbonylamino group preferably has from 7 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. One example of the aryloxycarbonylamino group is a phenoxycarbonylamino group.

[0059]

The alkylsulfonylamino and arylsulfonylamino group means to include substituted alkylsulfonylamino and arylsulfonylamino groups and unsubstituted alkylsulfonylamino and arylsulfonylamino groups. The sulfonylamino group preferably has from 1 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. Examples of the sulfonylamino groups are methylsulfonylamino, N-phenyl-methylsulfonylamino,

phenylsulfonylamino and 3-carboxyphenylsulfonylamino groups.

[0060]

The heterocyclic sulfonylamino group means to include a substituted heterocyclic sulfonylamino group and an unsubstituted heterocyclic sulfonylamino group. The heterocyclic sulfonylamino group preferably has from 1 to 12 carbon atoms. One example of the substituent is an ionic hydrophilic group. Examples of the heterocyclic sulfonylamino group are 2-thiophenesulfonylamino and 3-pyridinesulfonylamino groups.

[0061]

The heterocyclic sulfonyl group means to include a substituted heterocyclic sulfonyl group and an unsubstituted heterocyclic sulfonyl group. The heterocyclic sulfonyl group preferably has from 1 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. Examples of the heterocyclic sulfonyl group are 2-thiophenesulfonyl and 3-pyridinesulfonyl groups.

[0062]

The heterocyclic sulfinyl group means to include a substituted heterocyclic sulfinyl group and an unsubstituted heterocyclic sulfinyl group. The heterocyclic sulfinyl group preferably has from 1 to 20

carbon atoms. One example of the substituent is an ionic hydrophilic group. One example of the heterocyclic sulfinyl group is a 4-pyridinesulfinyl group.

[0063]

The alkylthio, arylthio and heterocyclic-thio group means to include substituted alkylthio, arylthio and heterocyclic-thio groups and unsubstituted alkylthio, arylthio and heterocyclic-thio groups. The alkylthio, arylthio and heterocyclic-thio group preferably has from 1 to 20 carbon atoms. One example of the substituent is an ionic hydrophilic group. Examples of the alkylthio, arylthio and heterocyclic-thio groups are methylthio, phenylthio and 2-pyridylthio groups.

[0064]

The alkylsulfonyl and arylsulfonyl group means to include substituted alkylsulfonyl and arylsulfonyl groups, and unsubstituted alkylsulfonyl and arylsulfonyl groups. Examples of the alkylsulfonyl and arylsulfonyl groups are methylsulfonyl and phenylsulfonyl groups.

[0065]

The alkylsulfinyl and arylsulfinyl group means to include substituted alkylsulfinyl and arylsulfinyl groups, and unsubstituted alkylsulfinyl and arylsulfinyl groups. Examples of the alkylsulfinyl and arylsulfinyl groups are methylsulfinyl and phenylsulfinyl groups.

[0066]

The sulfamoyl group means to include a substituted sulfamoyl group and an unsubstituted sulfamoyl group. One example of the substituent is an alkyl group. Examples of the sulfamoyl group are dimethylsulfamoyl and di(2-hydroxyethyl)sulfamoyl groups.

[0067]

Formulae (1), (1-A) and (1-B) are further described.

In the following description, those described hereinabove shall apply to the groups and the substituents.

In formula (1), A_{41} , B_{41} and C_{41} each independently represent an optionally-substituted aromatic group (A_{41} and C_{41} each are a monovalent aromatic group such as an aryl group; B_{41} is a divalent aromatic group such as an arylene group), or an optionally substituted heterocyclic group (A_{41} and C_{41} each are a monovalent heterocyclic group; B_{41} is a divalent heterocyclic group). Examples of the aromatic ring are benzene and naphthalene rings; and the hetero atom to form the hetero ring includes N, O and S. The hetero ring may be condensed with an aliphatic ring, an aromatic ring or any other hetero ring.

The substituent may be an arylazo group or a heterocyclic azo group.

Preferably, at least one of A_{41} , B_{41} and C_{41} is a

heterocyclic group. More preferably, at least two of A₄₁, B₄₁ and C₄₁ are heterocyclic groups. All of A₄₁, B₄₁ and C₄₁ may be heterocyclic groups.

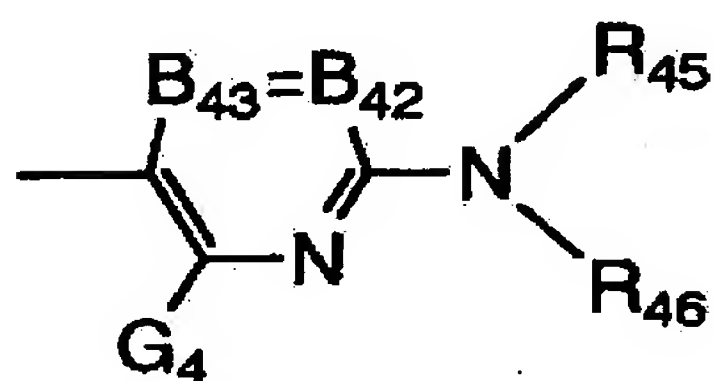
[0068]

Preferably, the heterocyclic group for C₄₁ is an aromatic, nitrogen-containing 6-membered heterocyclic group represented by the following formula (1-C). More preferably, C₄₁ is an aromatic, nitrogen-containing 6-membered heterocyclic group represented by the following formula (1-C). In this case, formula (1) corresponds to formula (1-A).

[0069]

formula (1-C)

[chem.3]



[0070]

In formula (1-C), B₄₂ and B₄₃ each represent =CR₄₁- and -CR₄₂=, or any one of them represents a nitrogen atom and the other represents =CR₄₁- or -CR₄₂=. Preferably, they represent =CR₄₁- and -CR₄₂=.

R₄₅ and R₄₆ each independently represent a hydrogen atom, an aliphatic group, an aromatic group, a

heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkyl or arylsulfonyl group, or a sulfamoyl group. These groups may be further substituted. Preferably, R_{45} and R_{46} each are a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, or an alkyl or arylsulfonyl group. More preferably, they are any of a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, or an alkyl or arylsulfonyl group; most preferably, any of a hydrogen atom, an aryl group or a heterocyclic group. The groups may be further substituted. R_{45} and R_{46} must not be hydrogen atoms at the same time.

[0071]

G_4 , R_{41} and R_{42} each independently represent a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic-oxycarbonyl group, an acyl group, a hydroxyl group, an alkoxy group, an aryloxy group, a heterocyclic-oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including alkylamino group, arylamino group, heterocyclic amino group), an acylamino group, an

ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkyl or arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkyl or arylthio group, a heterocyclic-thio group, an alkyl or arylsulfonyl group, a heterocyclic sulfonyl group, an alkyl or arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group, or a sulfo group, and each group may further be substituted.

[0072]

The substituent represented by G_4 is preferably a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a hydroxyl group, an alkoxy group, an aryloxy group, an acyloxy group, a heterocyclic-oxy group, an amino group (including alkylamino group, arylamino group, heterocyclic amino group), an acylamino group, an ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkyl or arylthio group, or a heterocyclic-thio group; more preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxyl group, an alkoxy group, an aryloxy group, an acyloxy group, an amino group (including alkylamino group, arylamino group, heterocyclic amino group), or an acylamino group; most preferably a hydrogen atom, an anilino group, or an acylamino group. These

groups may be further substituted.

[0073]

The substituent for R_{41} and R_{42} is preferably a hydrogen atom, an alkyl group, a halogen atom, an alkoxy carbonyl group, a carboxyl group, a carbamoyl group, a hydroxyl group, an alkoxy group, or a cyano group. These groups may be further substituted.

R_{41} and R_{45} , or R_{45} and R_{46} may bond to each other to form a 5- or 6-membered ring.

When the substituents represented by A_{41} , R_{41} , R_{42} , R_{45} , R_{46} and G_4 , are further substituted, the substituents include those mentioned hereinabove for the groups for G_4 , R_{41} and R_{42} . Preferably, the substituent includes an ionic hydrophilic group at any position of A_{41} , R_{41} , R_{42} , R_{45} , R_{46} and G_4 therein.

[0074]

The substituent, ionic hydrophilic group includes, for example, a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Preferably, the ionic hydrophilic group is a carboxyl group, a phosphono group or a sulfo group, more preferably a carboxyl group or a sulfo group. The carboxyl group, phosphono group and sulfo group may form salts. Examples of the counter ion to form the salts are ammonium ions, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion), and

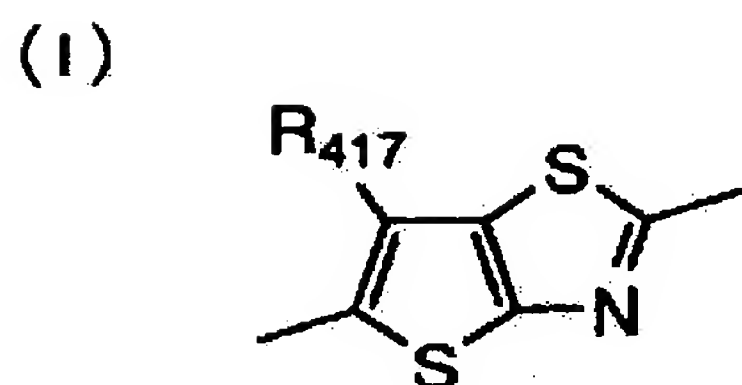
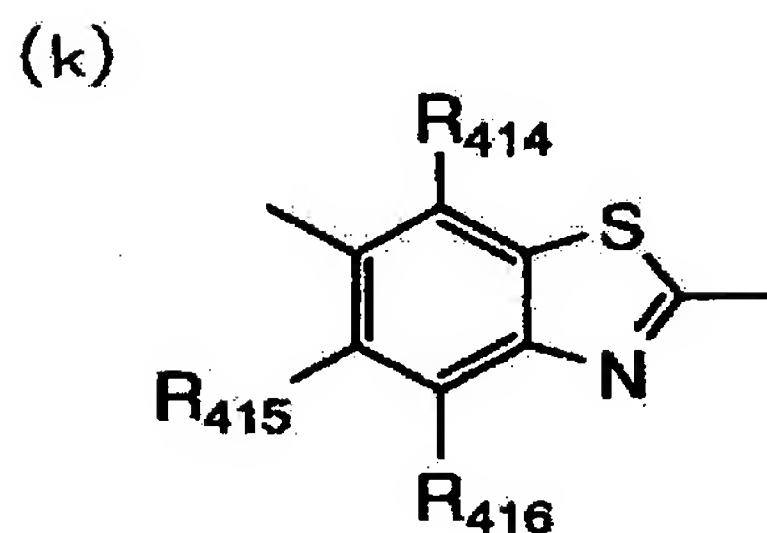
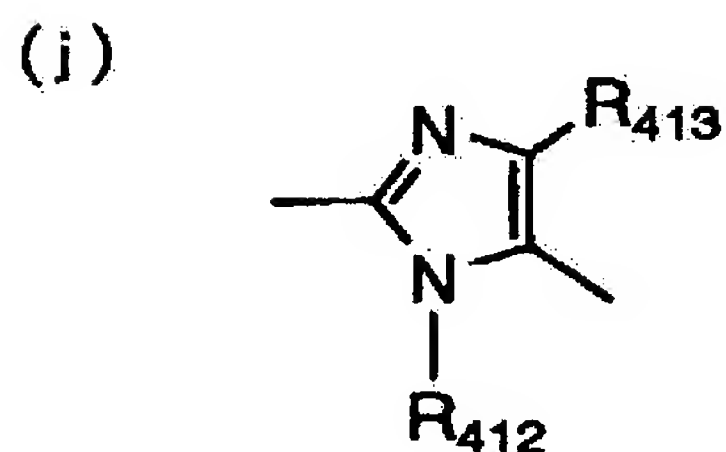
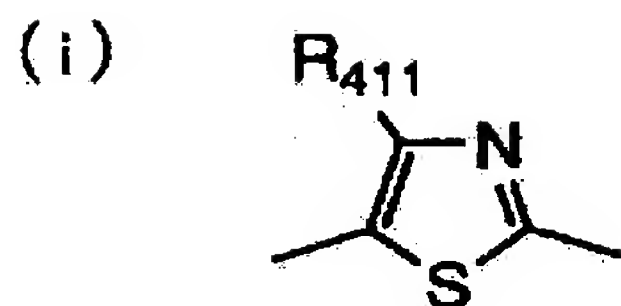
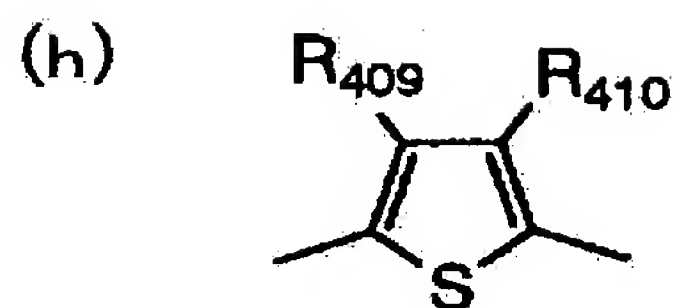
organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium ion). Among these, lithium ion is preferred.

[0075]

Preferred hetero rings for B₄₁ are thiophene, thiazole, imidazole, benzimidazole and thienothiazole rings when B₄₁ is a ring structure. These heterocyclic groups may be further substituted. Above all, especially preferred are thiophene, thiazole, imidazole, benzimidazole and thienothiazole rings represented by the following formulae (h) to (l). When B₄₁ is a thiophene ring (h) and when C₄₁ has the structure of formula (1-C), then formula (1) corresponds to formula (1-B).

[0076]

[chem.4]



[0077]

In formulae (h) to (l), R_{409} to R_{417} have the same meanings as those of the substituents of G_4 , and R_{42} in formula (1-A).

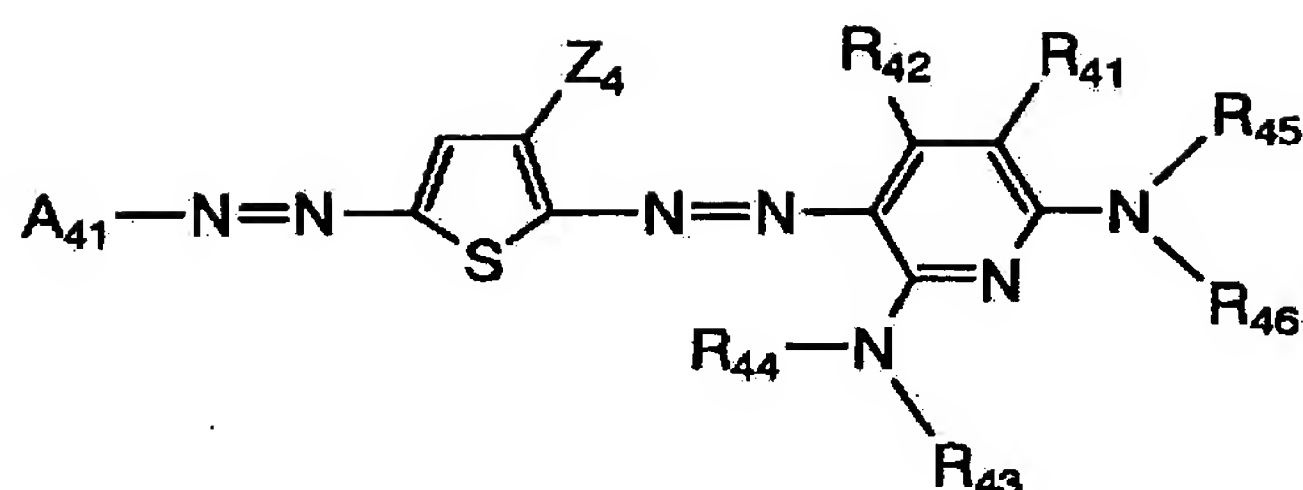
[0078]

Of dyes represented by formula (1-B), more preferred are the dyes having a structure represented by the following formula (1-D).

[0079]

Formula (1-D)

[chem.5]



[0080]

In formula, Z_4 represents an electron-attractive group having a Hammett's substituent constant σ_p of at least 0.20. Preferably, Z_4 is an electron-attractive group having σ_p of at least 0.30, more preferably at least 0.45, even more preferably at least 0.60, but not exceeding 1.0.

[0081]

Concretely, examples of the electron-attractive group having a Hammett's substituent constant σ_p of at least 0.60 are a cyano group, a nitro group, and an alkylsulfonyl group (e.g., methanesulfonyl, arylsulfonyl such as benzenesulfonyl).

[0082]

Examples of the electron-attractive group having a Hammett's substituent constant σ_p of at least 0.45 are, in addition to the groups mentioned above, an acyl group (e.g., acetyl), an alkoxycarbonyl group (e.g., dodecyloxycarbonyl), an aryloxycarbonyl group (e.g., m-chlorophenoxycarbonyl), an alkylsulfinyl group (e.g., n-propylsulfinyl), an arylsulfinyl group (e.g.,

phenylsulfinyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dimethylsulfamoyl), and a halogenoalkyl group (e.g., trifluoromethyl).

[0083]

Examples of the electron-attractive group having a Hammett's substituent constant σ_p of at least 0.30 are, in addition to the groups mentioned above, an acyloxy group (e.g., acetoxy), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibuthylcarbamoyl), a halogenoalkoxy group (e.g., trifluoromethoxy), a halogenoaryloxy group (e.g., pentafluorophenyloxy), a sulfonyloxy group (e.g., methylsulfonyloxy), a halogenoalkylthio group (e.g., difluoromethylthio), an aryl group substituted with at least two electron-attractive groups each having σ_p of at least 0.15 (e.g., 2,4-dinitrophenyl, pentachlorophenyl), and a heterocyclic group (e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl).

[0084]

Examples of the electron-attractive group having Hammett's substituent constant σ_p of at least 0.20 are, in addition to the groups mentioned above, a halogen atom.

[0085]

Above all, Z_4 is preferably any of an acyl group having from 2 to 20 carbon atoms, an alkyloxycarbonyl group having from 2 to 20 carbon atoms, a nitro group, a

cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms, an arylsulfonyl group having from 6 to 20 carbon atoms, a carbamoyl group having from 1 to 20 carbon atoms, or a halogenoalkyl group having from 1 to 20 carbon atoms; more preferably any of a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms, or an arylsulfonyl group having from 6 to 20 carbon atoms; most preferably a cyano group.

[0086]

R₄₁, R₄₂, R₄₅, and R₄₆ of formula (1-D) have the same meanings as in formula (1-A). R₄₃ and R₄₄ each independently represent a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkyl or arylsulfonyl group, or a sulfamoyl group; preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, or an alkyl or arylsulfonyl group; more preferably a hydrogen atom, an aromatic group or a heterocyclic group.

[0087]

The groups in formula (1-D) may be further substituted. When such groups are further substituted, the substituents include the substituents described in formula (1-A), the groups exemplified in G₄, R₄₁ and R₄₂, or ionic hydrophilic groups.

[0088]

Especially preferred combinations of the substituents in the azo dyes represented by formula (1-B) are mentioned below. R_{45} and R_{46} are preferably any of a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a sulfonyl group or an acyl group; more preferably any of a hydrogen atom, an aryl group, a heterocyclic group or a sulfonyl group; most preferably any of a hydrogen atom, an aryl group or a heterocyclic group. However, R_{45} and R_{46} must not be hydrogen atoms at the same time.

G_4 is preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxyl group, an amino group or an acylamino group, more preferably a hydrogen atom, a halogen atom, an amino group or an acylamino group, most preferably a hydrogen atom, an amino group or an acylamino group.

A_{41} is preferably a pyrazole ring, an imidazole ring, an isothiazole ring, a thiadiazole ring, a benzothiazole ring; most preferably a benzene ring or a naphthalene ring.

Also preferably, B_{42} and B_{43} are $=CR_{41}-$ and $-CR_{42}=$, respectively; and R_{41} and R_{42} are preferably any of a hydrogen atom, an alkyl group, a halogen atom, a cyano group, a carbamoyl group, a carboxyl group, a hydroxyl

group, an alkoxy group or an alkoxycarbonyl group, more preferably any of a hydrogen atom, an alkyl group, a carboxyl group, a cyano group or a carbamoyl group.

[0089]

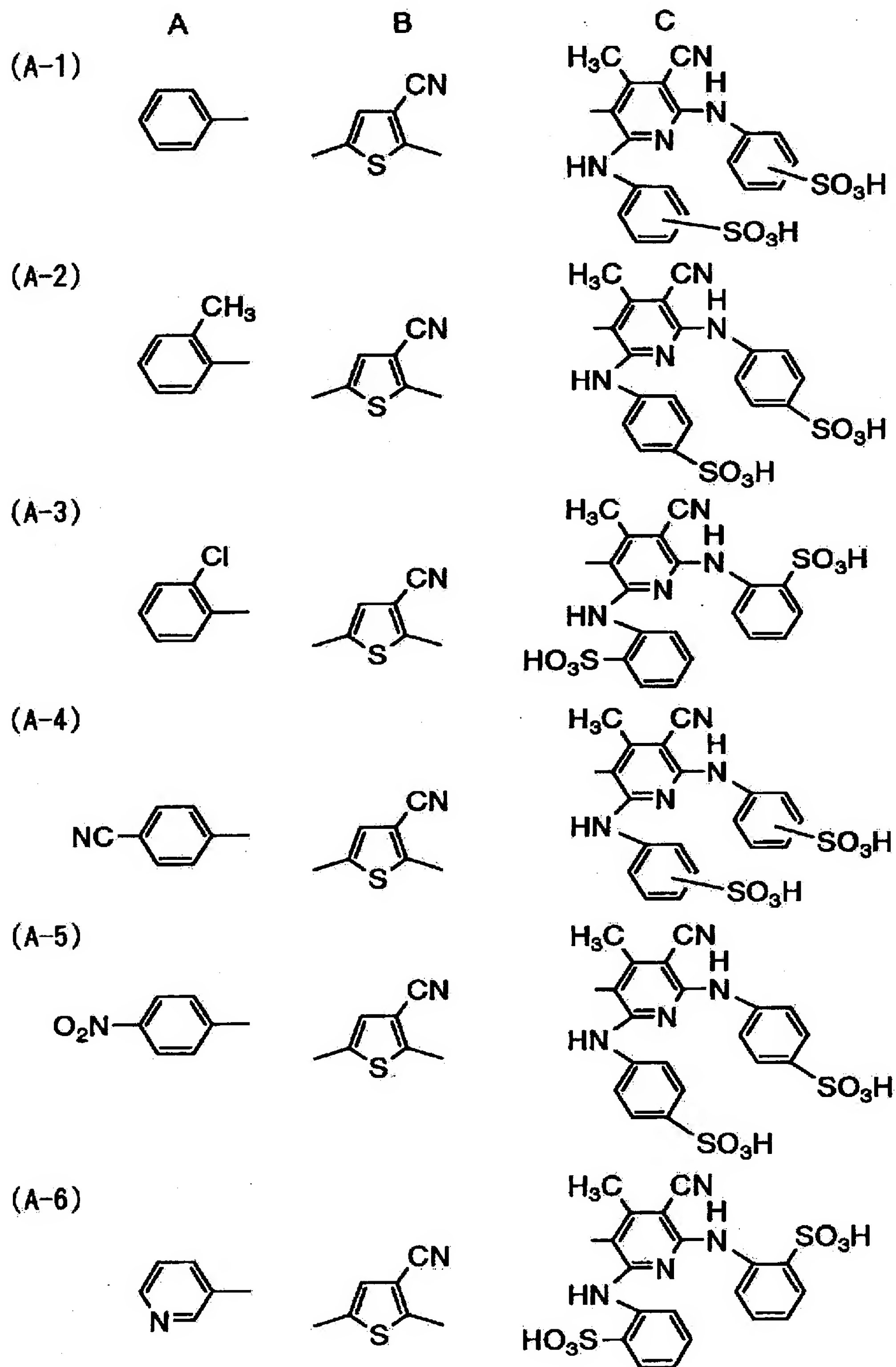
Regarding the preferred combinations of the substituents of the azo dyes, it is desirable that at least one of the substituents is the above-mentioned preferred group. More preferably, a larger number of the substituents are the preferred groups. Most preferably, all the substituents are the preferred groups.

[0090]

Specific examples of the azo dyes represented by formula (1) are mentioned below, to which, however, the invention should not be limited. In the following examples, the carboxyl group, the phosphono group and the sulfo group may form salts. Examples of the counter ion to form the salts are ammonium ions, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion), and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium ion). Of those, preferred is lithium ion.

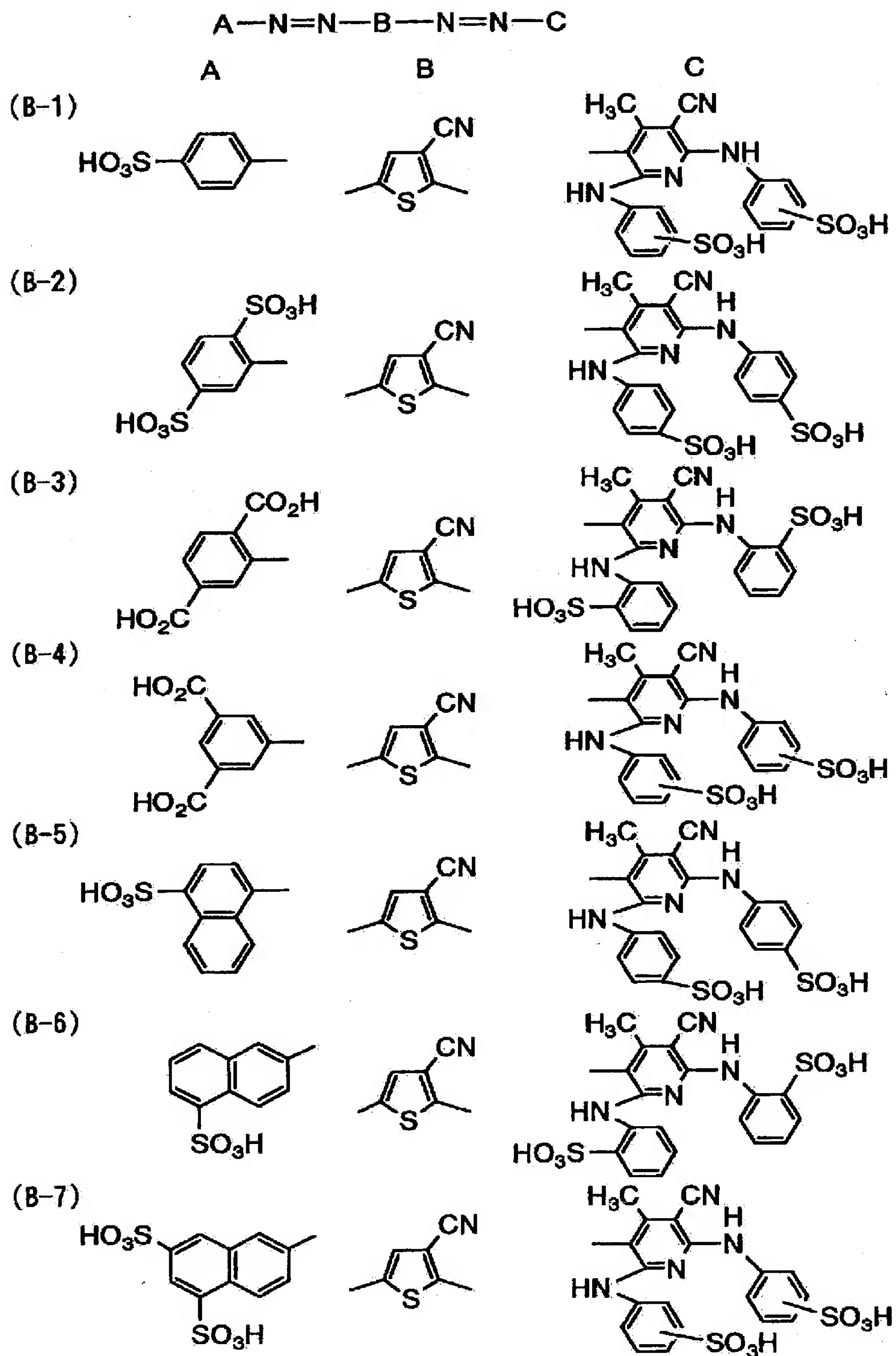
[0091]

[chem.6]



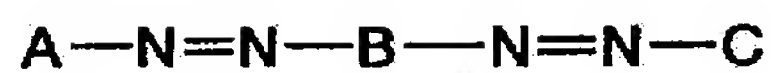
[0092]

[chem.7]



[0093]

[chem.8]

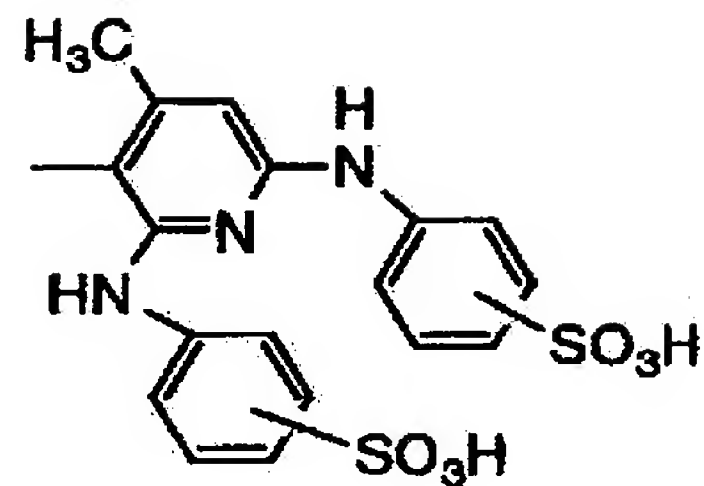
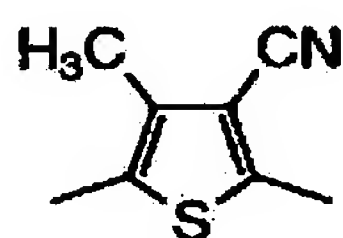
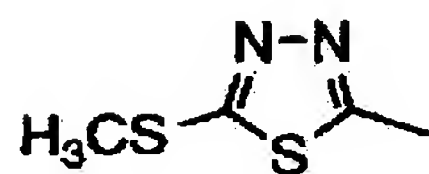


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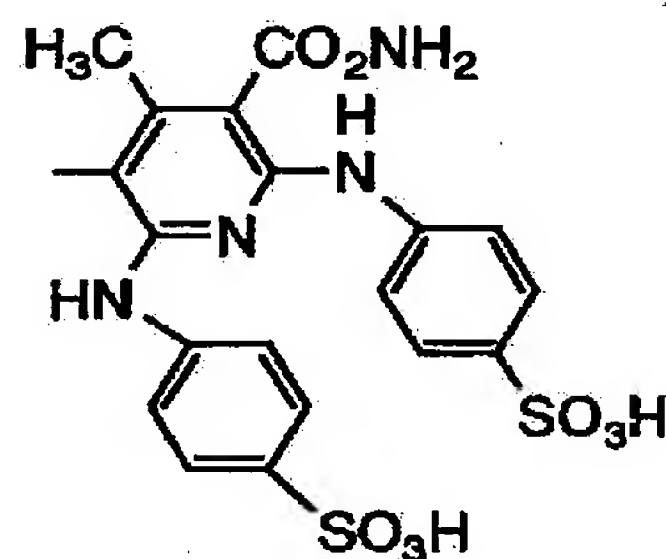
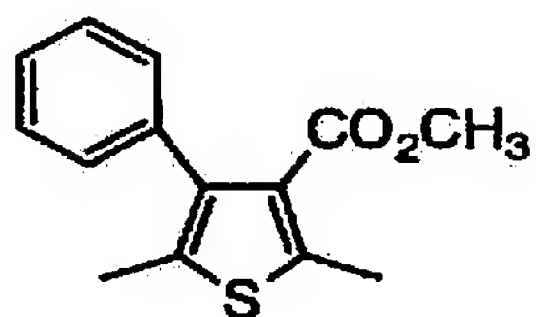
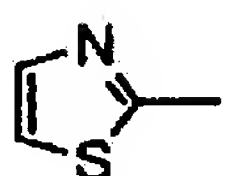
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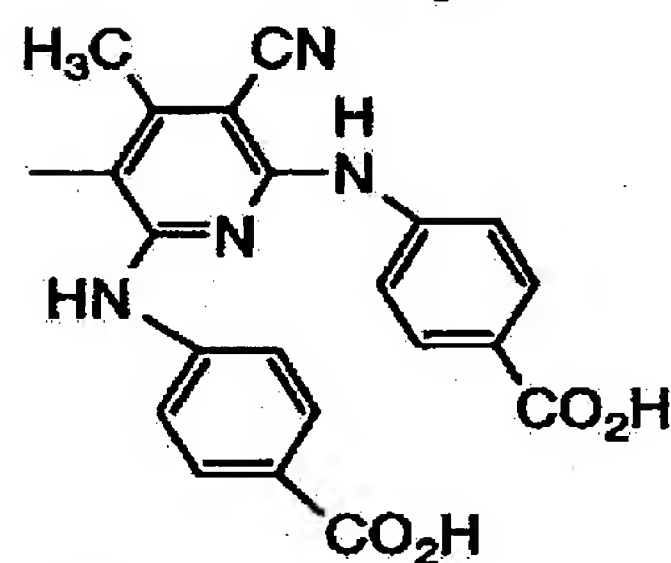
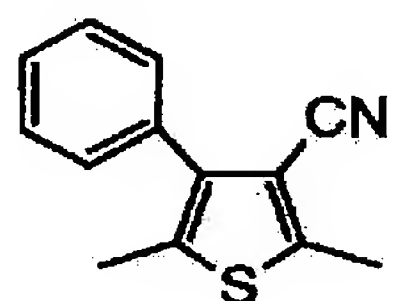
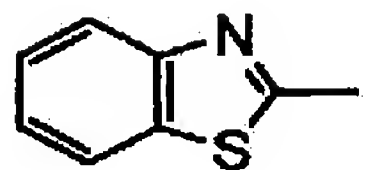
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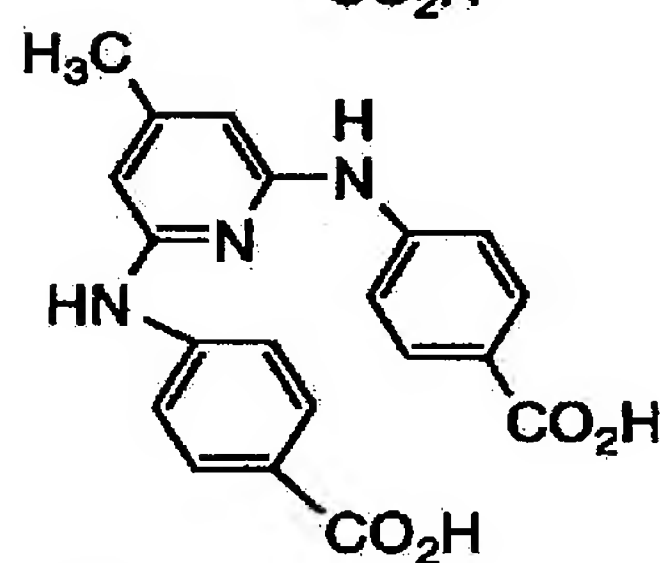
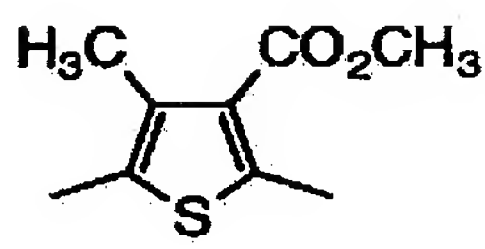
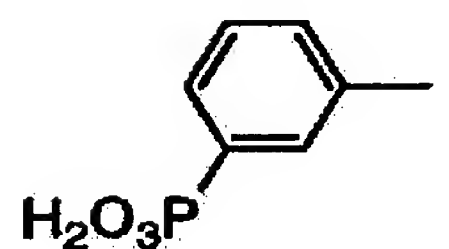
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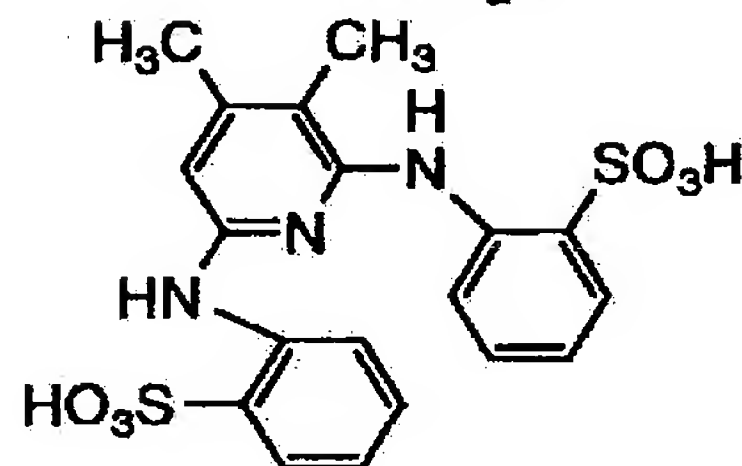
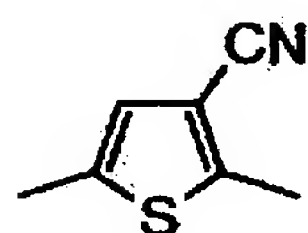
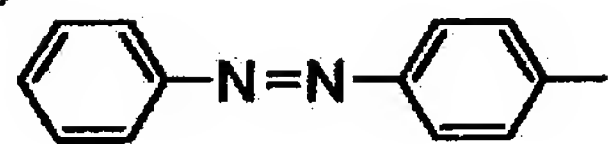
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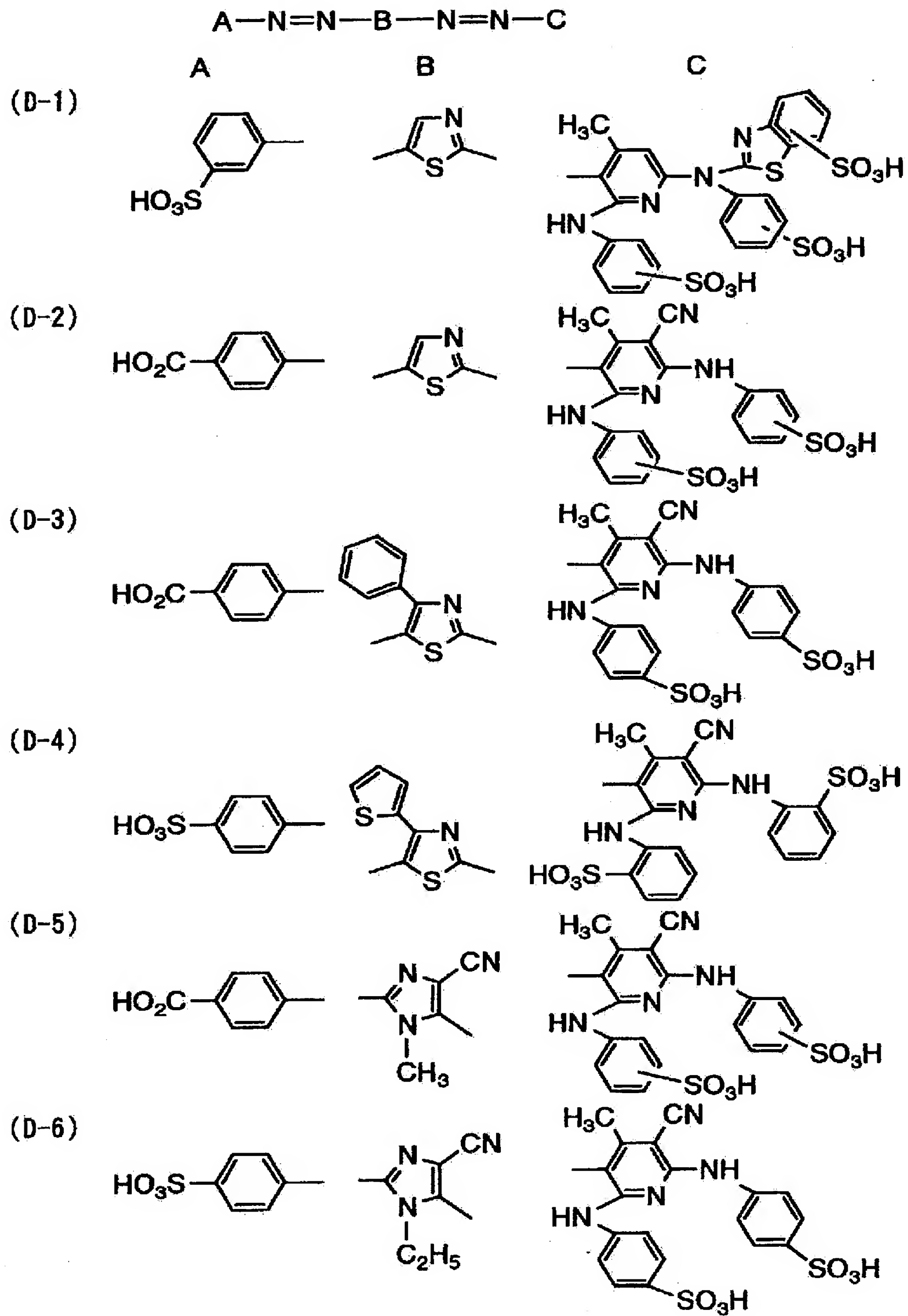


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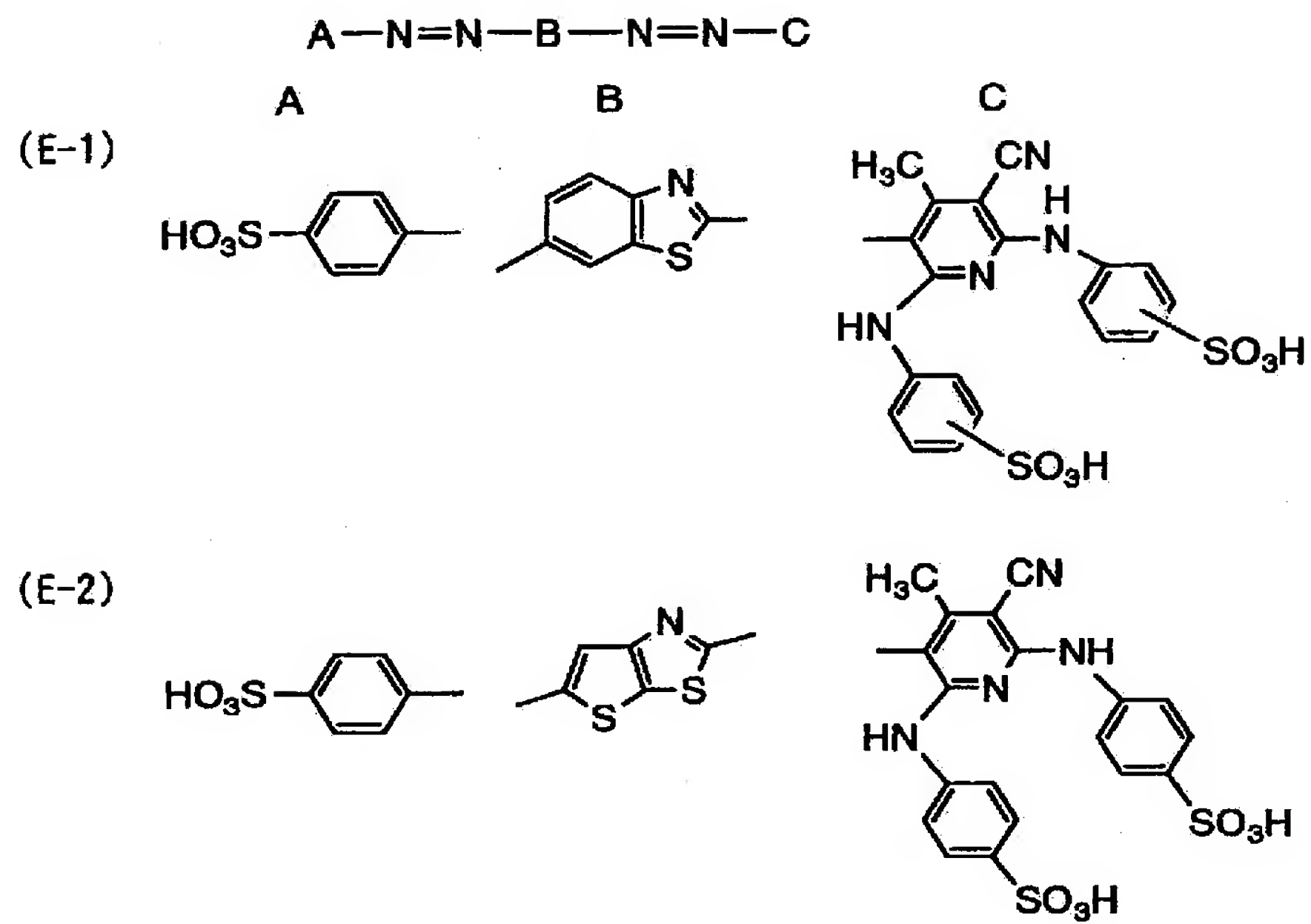
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[chem.9]



[0095]

[chem.10]



[0096]

[chem.11]

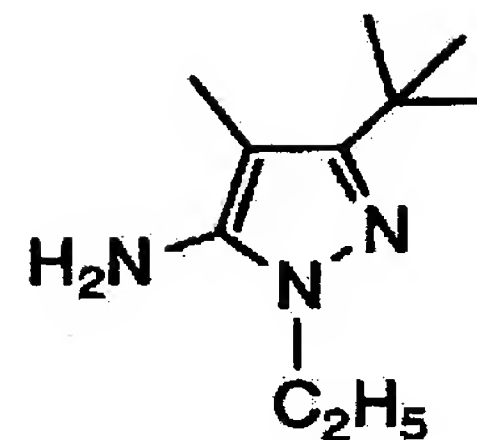
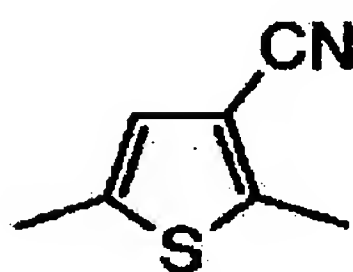
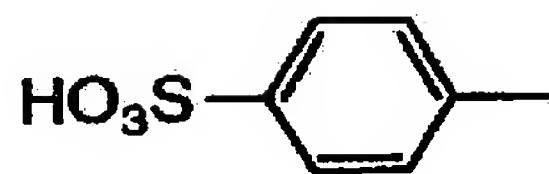


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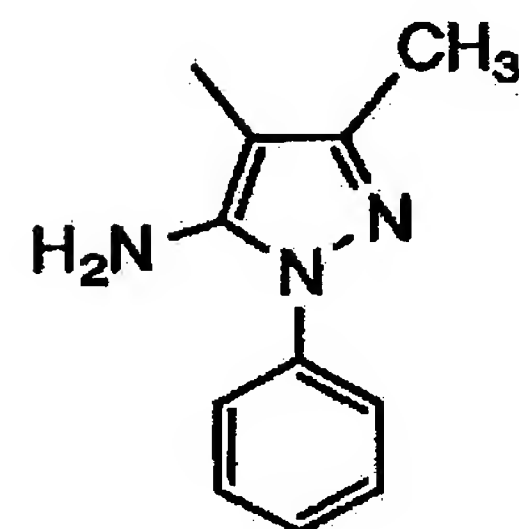
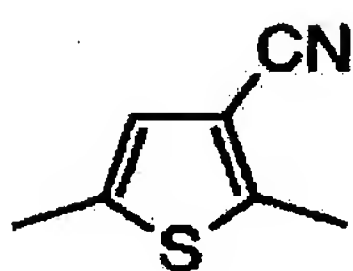
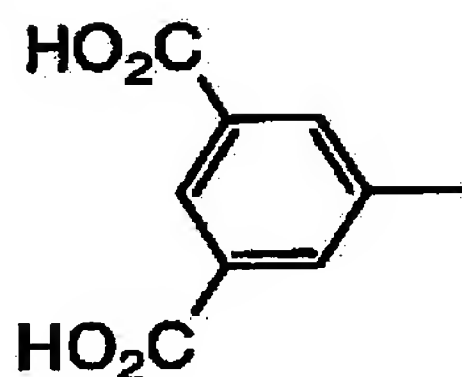
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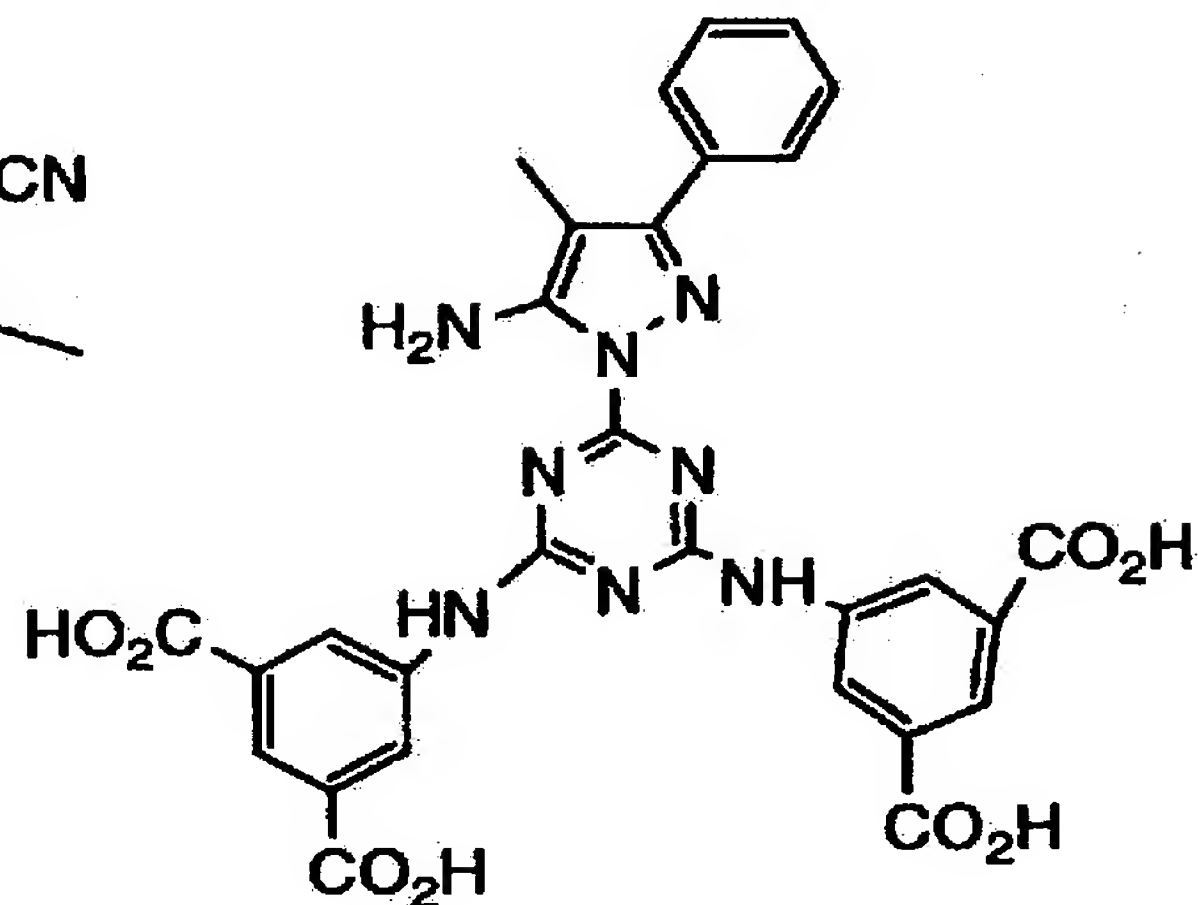
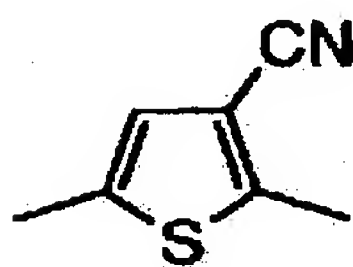
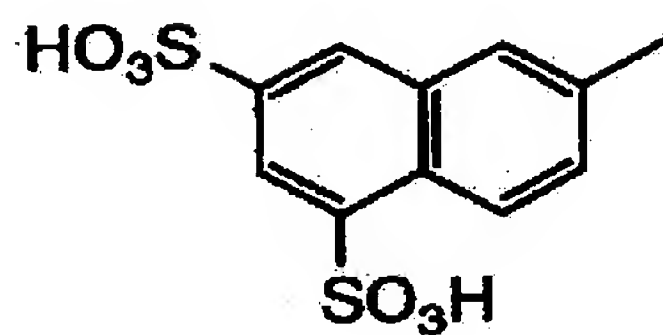
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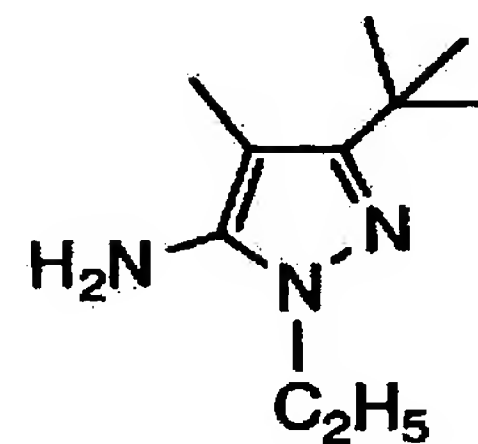
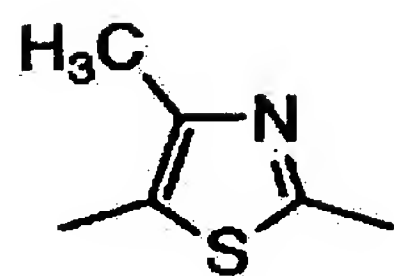
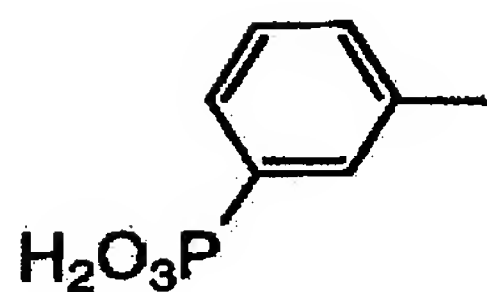
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(F-3)



(F-4)



[0097]

The azo dyes represented by formulae (1), (1-A), (1-B) and (1-D) may be produced through coupling reaction of

a diazo component with a coupling component. For it, for example, the methods described in JP-A 2002-113460 may be referred to.

[0098]

For the dyes (S) having λ_{\max} of from 350 nm to 500 nm, preferred are yellow dyes and yellow pigments described below. Dyes represented by formulae (1) and (2) in which n is 0 or y is 0 are usable for the dyes (S).

[0099]

Preferably, the content of the azo dye represented by formula (1) in the ink is from 0.2 to 20 % by mass, more preferably from 0.5 to 15 % by mass.

[0100]

Compounds of formula (2) are described in detail hereinunder.

formula (2) $P-(N=N-Q)_x-N=N-R$

[0101]

wherein P, Q and R each represent an optionally-substituted aromatic group (P and R each are a monovalent aromatic group such as an aryl group, Q is a divalent aromatic group such as an arylene group). In particular, Q is preferably a polycyclic aromatic ring such as a naphthalene ring.

[0102]

x is an integer of 1 or more, y is an integer of 0

or more. Preferably, $x = y = 1$.

[0103]

The substituents that may be in formula (2) are a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic-oxycarbonyl group, an acyl group, a hydroxyl group, an alkoxy group, an aryloxy group, a heterocyclic-oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including an alkylamino group, an arylamino group, a heterocyclic amino group), an acylamino group, an ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkyl or arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkyl or arylthio group, a heterocyclic-thio group, an alkyl or arylsulfonyl group, a heterocyclic sulfonyl group, an alkyl or arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group, and a sulfo group. These groups may be further substituted. Preferred examples of these substituents may be the same as those corresponding to the groups in formula (1). The substituent may also be an arylazo group.

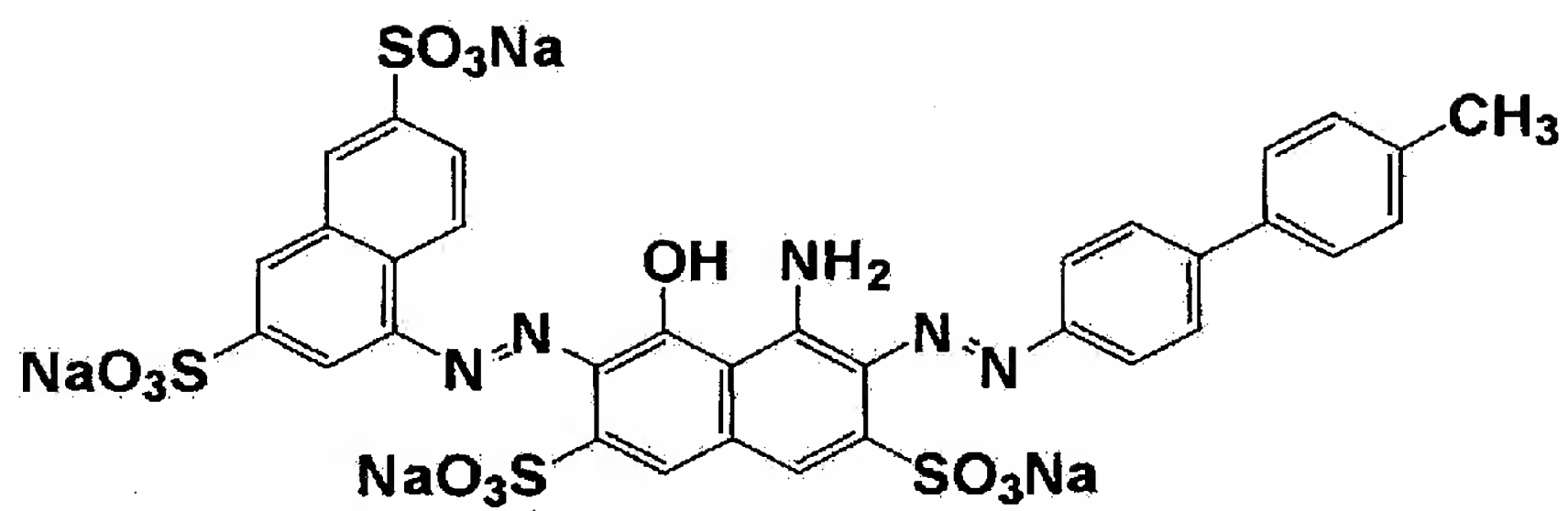
[0104]

Examples of the black dyes of formula (2) usable in the invention are mentioned below, to which, however, the invention should not be limited. In the following Examples, the sulfo group may form salts. Examples of the counter ion to form the salts are ammonium ions, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion), and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium ion). For the counter ion, preferred is lithium ion.

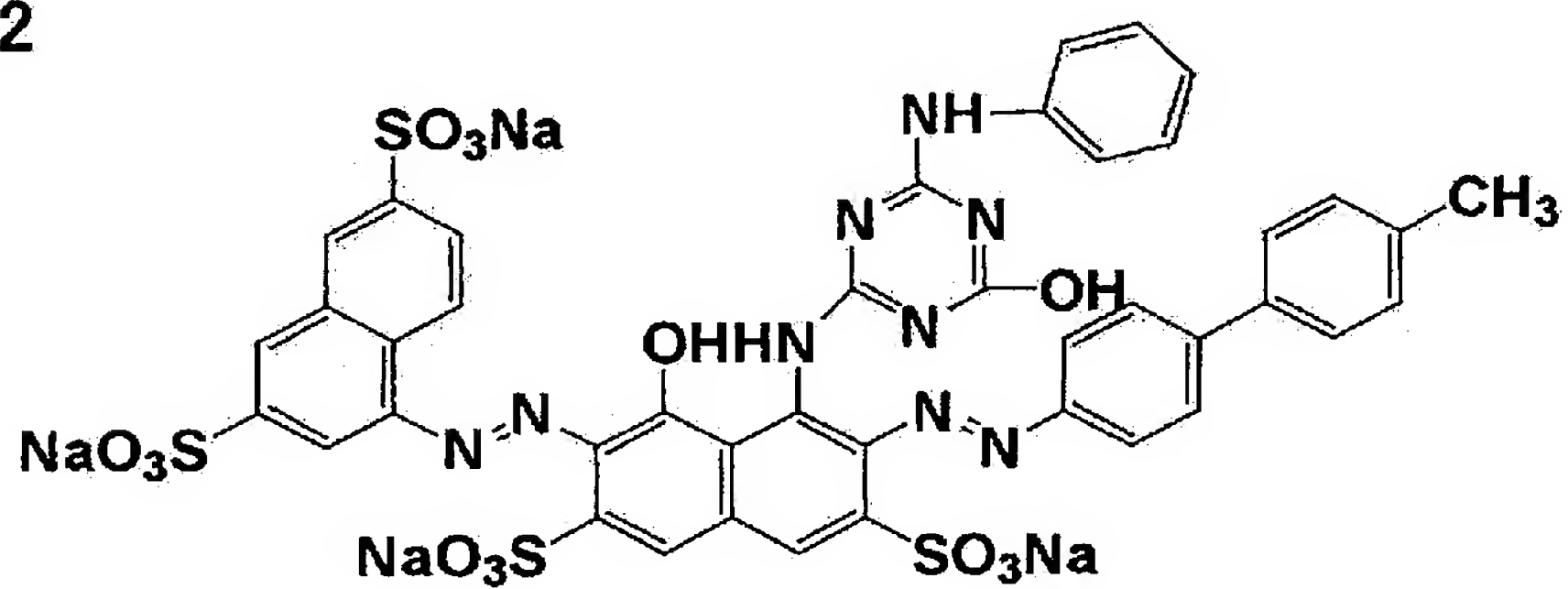
[0105]

[chem. 12]

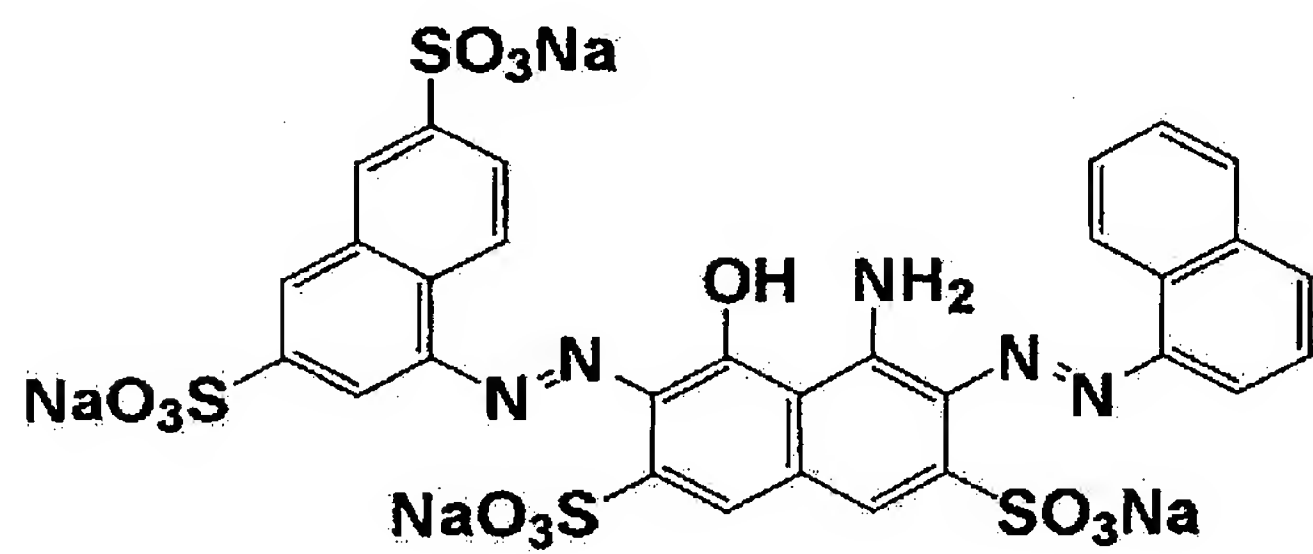
TS-1



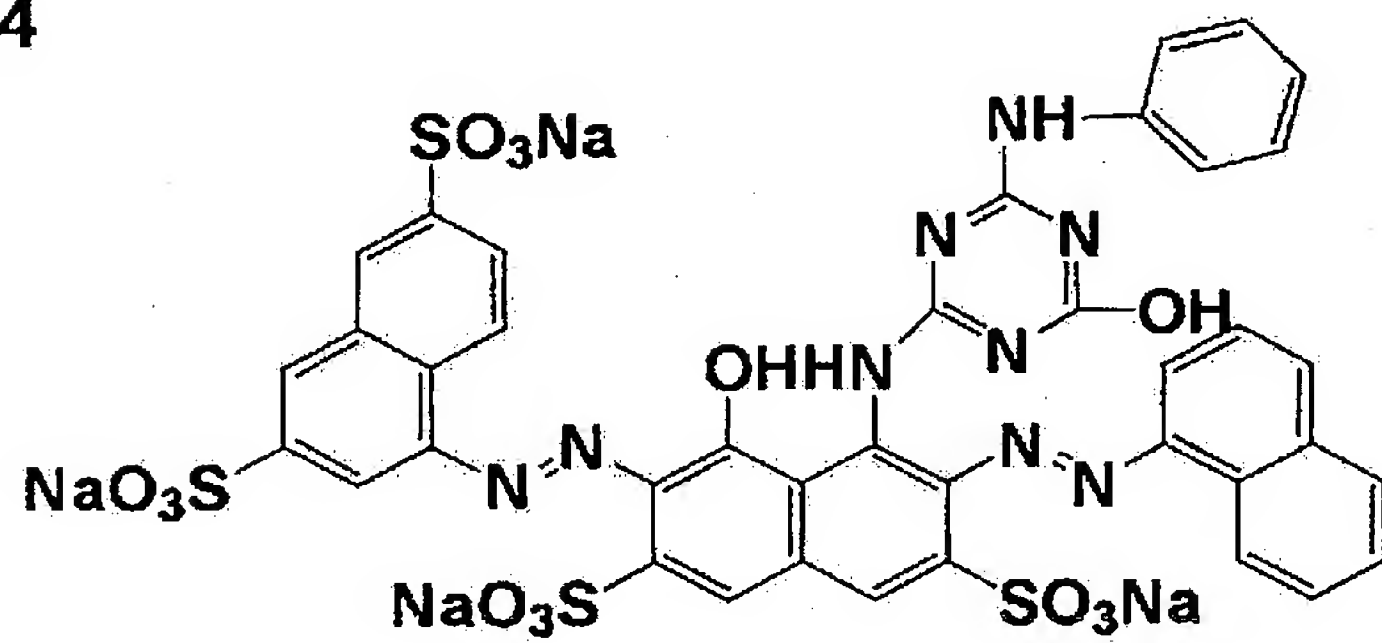
TS-2



TS-3



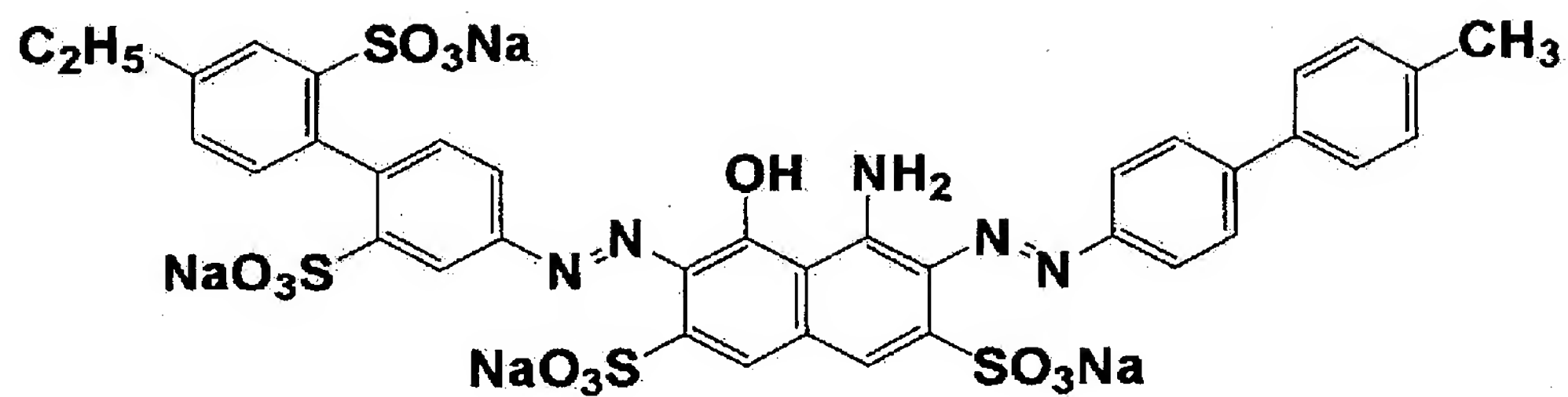
TS-4



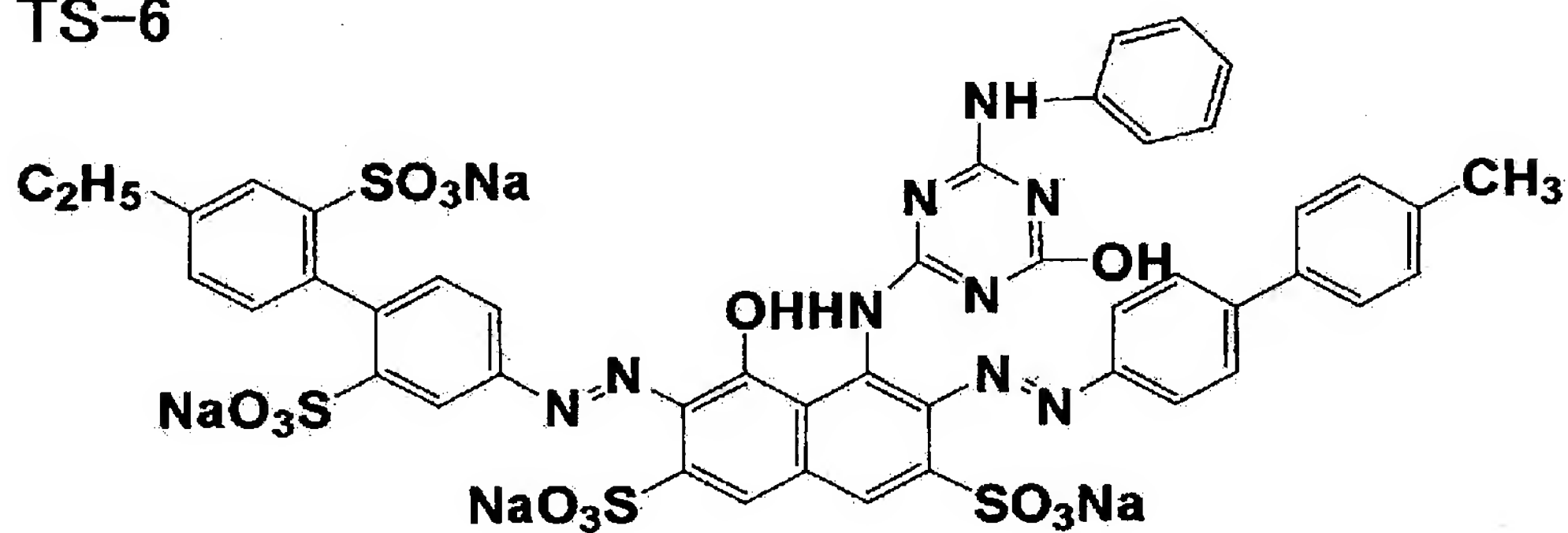
[0106]

[chem. 13]

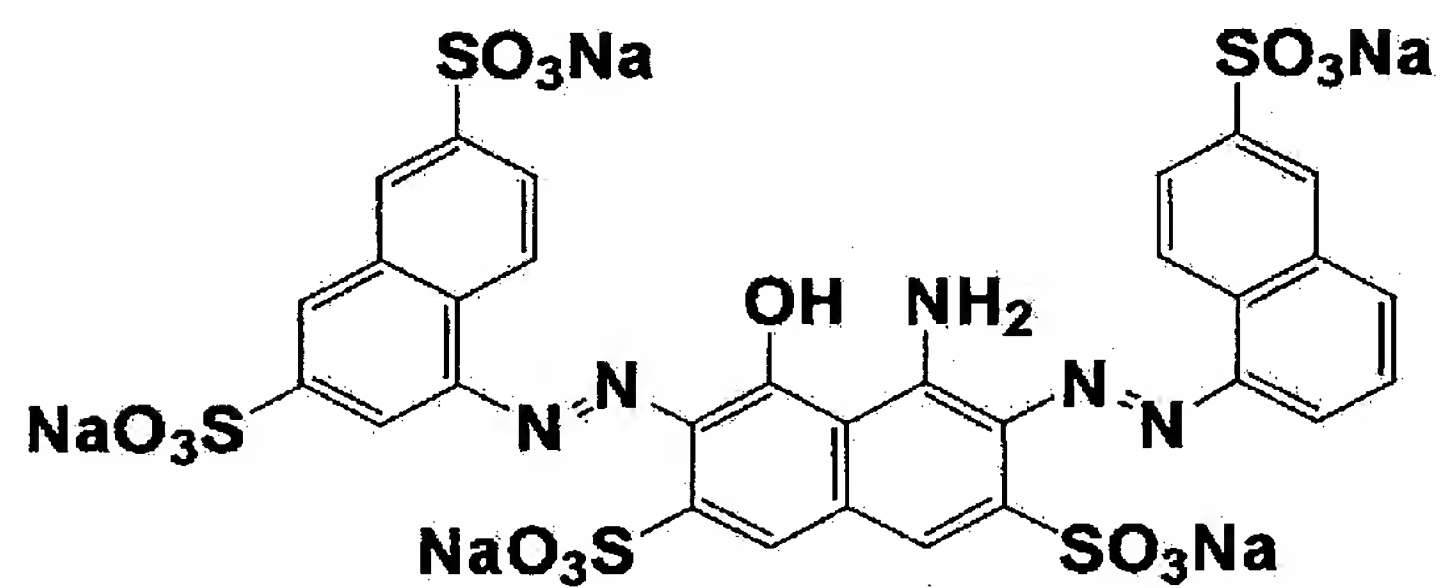
TS-5



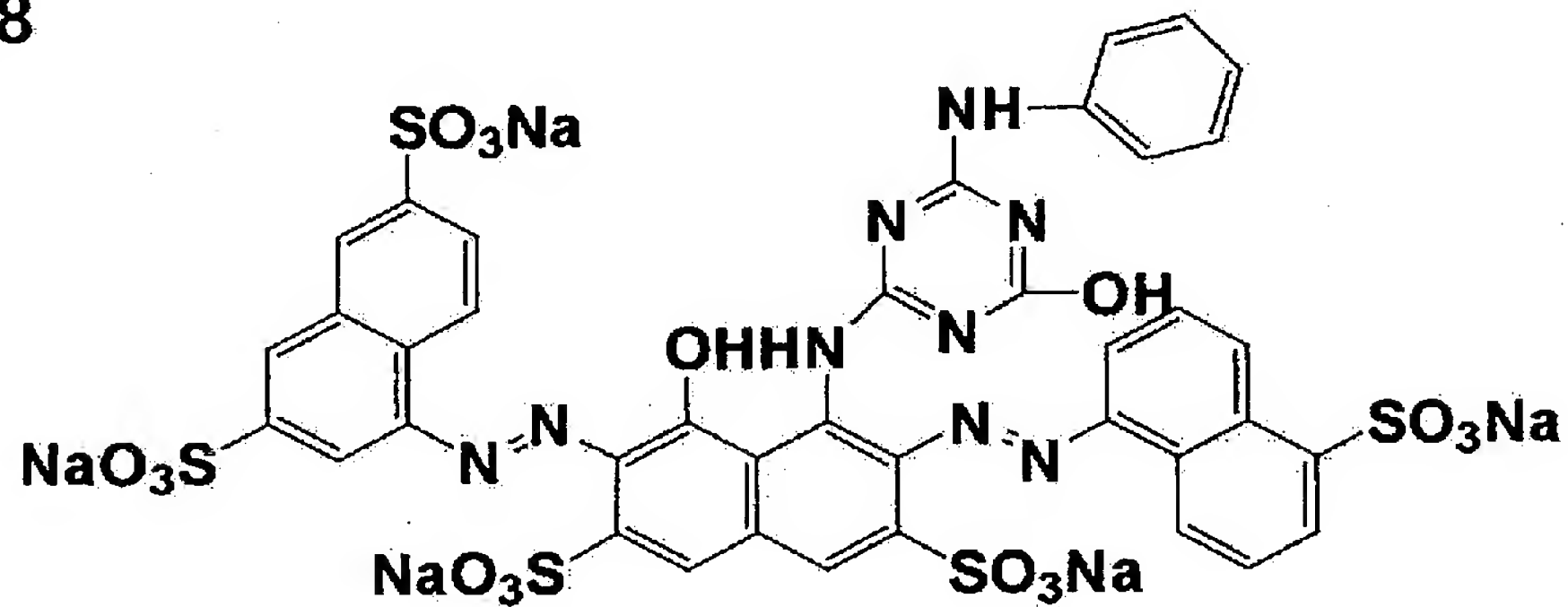
TS-6



TS-7



TS-8



[0107]

(Ink Set)

The ink set of the invention may contain any other dyes along with the above-mentioned dyes for full-color image formation or for color tone control. Examples of the additional dyes that may be used in the invention are mentioned below.

[0108]

Yellow dyes are, for example, aryl or heterylazo dyes having, as the coupling component thereof, phenols, naphthols, anilines, pyrazolones, pyridones or open-chain active methylene compounds; azomethine dyes having, as the coupling component thereof, open-chain active methylene compounds; methine dyes such as benzylidene dyes, monomethine-oxonole dyes; quinone dyes such as naphthoquinone dyes, anthraquinone dyes. Other dye species than these are quinophthalone dyes, nitro-nitroso dyes, acridine dyes, and acridinone dyes. These dyes may present yellow only after a part of the chromophore thereof has been dissociated. In such a case, the counter cation may be an inorganic cation such as alkali metal or ammonium ion, or an organic cation such as pyridinium or quaternary ammonium salt, or may also be a polymer cation having any of these as a partial structure thereof.

[0109]

Magenta dyes are, for example, aryl or heterylazo dyes having, as the coupling component thereof, phenols, naphthols or anilines; azomethine dyes having, as the coupling component thereof, pyrazolones or pyrazolotriazoles; methine dyes such as arylidene dyes, styryl dyes, merocyanine dyes, oxonole dyes; carbonium dyes such as diphenylmethane dyes, triphenylmethane dyes, xanthene dyes; quinone dyes such as naphthoquinone dyes, anthraquinone dyes, anthrapyridone dyes; and condensed polycyclic dyes such as dioxazine dyes. These dyes may present magenta only after a part of the chromophore thereof has been dissociated. In such a case, the counter cation may be an inorganic cation such as alkali metal or ammonium ion, or an organic cation such as pyridinium or quaternary ammonium salt, or may also be a polymer cation having any of these as a partial structure thereof.

[0110]

Cyan dyes are, for example, azomethine dyes such as indaniline dyes, indophenol dyes; polymethine dyes such as cyanine dyes, oxonole dyes, merocyanine dyes; carbonium dyes such as diphenylmethane dyes, triphenylmethane dyes, xanthene dyes; phthalocyanine dyes; anthraquinone dyes; aryl or heterylazo dyes having,

as the coupling component thereof, phenols, naphthols or anilines; and indigo and thioindigo dyes. These dyes may present cyan only after a part of the chromophore thereof has been dissociated. In such a case, the counter cation may be an inorganic cation such as alkali metal or ammonium ion, or an organic cation such as pyridinium or quaternary ammonium salt, or may also be a polymer cation having any of these as a partial structure thereof.

Further, black dyes such as polyazo dyes may also be used.

[0111]

In addition, water-soluble dyes such as direct dyes, acid dyes, edible dyes, basic dyes and reactive dyes may also be used herein. Above all, especially preferred are the following:

C.I. Direct Red 2, 4, 9, 23, 26, 31, 39, 62, 63, 72, 75, 76, 79, 80, 81, 83, 84, 89, 92, 95, 111, 173, 184, 207, 211, 212, 214, 218, 21, 223, 224, 225, 226, 227, 232, 233, 240, 241, 242, 243, 247;

C.I. Direct Violet 7, 9, 47, 48, 51, 66, 90, 93, 94, 95, 98, 100, 101;

C.I. Direct Yellow 8, 9, 11, 12, 27, 28, 29, 33, 35, 39, 41, 44, 50, 53, 58, 59, 68, 86, 87, 93, 95, 96, 98, 100, 106, 108, 109, 110, 130, 132, 142, 144, 161, 163;

C.I. Direct Blue 1, 10, 15, 22, 25, 55, 67, 68, 71, 76,

77, 78, 80, 84, 86, 87, 90, 98, 106, 108, 109, 151, 156,
 158, 159, 160, 168, 189, 192, 193, 194, 199, 200, 201,
 202, 203, 207, 211, 213, 214, 218, 225, 229, 236, 237,
 244, 248, 249, 251, 252, 264, 270, 280, 288, 289, 291;
 C.I. Direct Black 9, 17, 19, 22, 32, 51, 56, 62, 69, 77,
 80, 91, 94, 97, 108, 112, 113, 114, 117, 118, 121, 122,
 125, 132, 146, 154, 166, 168, 173, 199;
 C.I. Acid Red 35, 42, 52, 57, 62, 80, 82, 111, 114, 118,
 119, 127, 128, 131, 143, 151, 154, 158, 249, 254, 257,
 261, 263, 266, 289, 299, 301, 305, 336, 337, 361, 396,
 397;
 C.I. Acid Violet 5, 34, 43, 47, 48, 90, 103, 126;
 C.I. Acid Yellow 17, 19, 23, 25, 39, 40, 42, 44, 49, 50,
 61, 64, 76, 79, 110, 127, 135, 143, 151, 159, 169, 174,
 190, 195, 196, 197, 199, 218, 219, 222, 227;
 C.I. Acid Blue 9, 25, 40, 41, 62, 72, 76, 78, 80, 82, 92,
 106, 112, 113, 120, 127:1, 129, 138, 143, 175, 181, 205,
 207, 220, 221, 230, 232, 247, 258, 260, 264, 271, 277,
 278, 279, 280, 288, 290, 326;
 C.I. Acid Black 7, 24, 29, 48, 52:1, 172;
 C.I. Reactive Red 3, 13, 17, 19, 21, 22, 23, 24, 29, 35,
 37, 40, 41, 43, 45, 49, 55;
 C.I. Reactive Violet 1, 3, 4, 5, 6, 7, 8, 9, 16, 17, 22,
 23, 24, 26, 27, 33, 34;
 C.I. Reactive Yellow 2, 3, 13, 14, 15, 17, 18, 23, 24, 25,

26, 27, 29, 35, 37, 41, 42;

C.I. Reactive Blue 2, 3, 5, 8, 10, 13, 14, 15, 17, 18, 19, 21, 25, 26, 27, 28, 29, 38;

C.I. Reactive Black 4, 5, 8, 14, 21, 23, 26, 31, 32, 34;

C.I. Basic Red 12, 13, 14, 15, 18, 22, 23, 24, 25, 27, 29, 35, 36, 38, 39, 45, 46;

C.I. Basic Violet 1, 2, 3, 7, 10, 15, 16, 20, 21, 25, 27, 28, 35, 37, 39, 40, 48;

C.I. Basic Yellow 1, 2, 4, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 39, 40;

C.I. Basic Blue 1, 3, 5, 7, 9, 22, 26, 41, 45, 46, 47, 54, 57, 60, 62, 65, 66, 69, 71;

C.I. Basic Black 8.

[0112]

Pigments and dyes may be combined in the ink of the invention.

The pigments usable in the ink of the invention are commercially-available ones and any other known ones described in various references. The references are, for example, *Color Index* (by the Society of Dyers and Colorists); *Revised New Version, Pigment Handbook* (by Nippon Pigment Technology Association, 1989); *Latest Pigment Application Technology* (by CMC Publishing, 1986); *Printing Ink Technology* (by CMC Publishing, 1984); W. Herbst & K. Hunger, *Industrial Organic Pigments* (by VCH

Verlagsgesellschaft, 1993). Concretely, organic pigments are azo pigments (azo-lake pigments, insoluble azo pigments, condensed azo pigments, chelate-azo pigments), polycyclic pigments (phthalocyanine pigments, anthraquinone pigments, perylene and perinone pigments, indigo pigments, quinacridone pigments, dioxazine pigments, isoindolinone pigments, quinophthalone pigments, diketopyrrolopyrrole pigments), dyeing lake pigments (lake pigments of acid or basic dyes), and azine pigments; and inorganic pigments are yellow pigments such as C.I. Pigment Yellow 34, 37, 42, 53; red pigments such as C.I. Pigment Red 101, 108; blue pigments such as C.I. Pigment Blue 27, 29, 17:1; black pigments such as C.I. Pigment Black 7, magnetite; and white pigments such as C.I. Pigment White 4, 6, 18, 21.

[0113]

Pigments preferred for color image formation are blue or cyan pigments such as phthalocyanine pigments, anthraquinone-based indanthrone pigments (e.g., C.I. Pigment Blue 60), and dyeing lake pigments such as triarylcarbonium pigments. Especially preferred are phthalocyanine pigments, and their preferred examples are copper phthalocyanines such as C.I. Pigment Blue 15:1, 15:2, 15:3, 15:4, 15:6; monochloro or low-chloro-copper phthalocyanines, aluminium phthalocyanines such as those

in EP 860475; non-metal phthalocyanine, C.I. Pigment Blue 16; and phthalocyanines with a center metal atom of Zn, Ni or Ti. Most preferred are C.I. Pigment Blue 15:3, 15:4, and aluminium phthalocyanines.

[0114]

Red to violet pigments are azo dyes (preferably C.I. Pigment Red 3, 5, 11, 22, 38, 48:1, 48:2, 48:3, 48:4, 49:1, 52:1, 53:1, 57:1, 63:2, 144, 146, 184; more preferably C.I. Pigment Red 57:1, 146, 184); quinacridone pigments (preferably C.I. Pigment Red 122, 192, 202, 207, 209, C.I. Pigment Violet 19, 42; more preferably C.I. Pigment Red 122); dyeing lake pigments such as triarylcarbonium pigments (preferably xanthene-type C.I. Pigment Red 81:1, C.I. Pigment Violet 1, 2, 3, 27, 39); dioxazine pigments (e.g., C.I. Pigment Violet 23, 37); diketopyrrolopyrrole pigments (e.g., C.I. Pigment Red 254); perylene pigments (e.g., C.I. Pigment Violet 29); anthraquinone pigments (e.g., C.I. Pigment Violet 5:1, 31, 33); thioindigo pigments (e.g., C.I. Pigment Red 38, 88).

[0115]

Yellow pigments are azo pigments (preferably monoazo pigments such as C.I. Pigment Yellow 1, 3, 74, 98; disazo pigments such as C.I. Pigment Yellow 12, 13, 14, 16, 17, 83; general azo pigments such as C.I. Pigment Yellow 93, 94, 95, 128, 155; benzimidazolone pigments such as C.I.

Pigment Yellow 120, 151, 154, 156, 180; more preferably those not using benzidine compounds for their starting material); isoindoline or isoindolinone pigments (preferably C.I. Pigment Yellow 109, 110, 137, 139); quinophthalone pigments (preferably C.I. Pigment Yellow 138); flavanthrone pigments (e.g., C.I. Pigment Yellow 24).

[0116]

Black pigments are inorganic pigments (preferably carbon black, magnetite) and aniline black. In addition to these, orange pigments (e.g., C.I. Pigment Orange 13, 16) and green pigments (e.g., C.I. Pigment Green 7) are also usable herein.

[0117]

The pigments usable in the ink of the invention may be the above-mentioned nude pigments or may be surface-treated ones. For their surface treatment, the pigments may be coated with resin or wax, or surfactant may be applied to the pigments, or a reactive substance (e.g., radical from silane coupling agent, epoxy compound, polyisocyanate, diazonium salt) may be bound to the pigment surface. These are described, for example, in the following references and patent publications.

<1> *Properties and Applications of Metal Soap* (by Miyuki Publishing),

- <2> *Printing Ink* (by CMC Publishing, 1984),
- <3> *Latest Pigment Application Technology* (by CMC Publishing, 1986),
- <4> USP 5,554,739, 5,571,311,
- <5> JP-A 9-151342, 10-140065, 10-292143, 11-166145.

In particular, self-dispersible pigments prepared by reacting a diazonium salt with carbon black as in the US patents of above <4>, and capsulated pigments prepared according to the methods in the Japanese patent publications of above <5> are effective, since they are stably dispersed in ink not requiring any superfluous dispersant.

[0118]

In the invention, the pigments may be dispersed by the use of a dispersant. Depending on the pigments to be used, various known dispersants may be used. For example, surfactant-type low-molecular dispersants or polymer-type dispersants may be used. Examples of the dispersants usable herein are described in, for example, JP-A 3-69949, and EP 549486. When the dispersant is used, a pigment derivative that is referred to as a synergist may be added thereto for promoting the dispersant adsorption by pigment.

The particle size of the pigment usable in the ink of the invention is preferably from 0.01 to 10 μm , more

preferably from 0.05 to 1 μm , in terms of the size of the dispersed particles.

For pigment dispersion, employable is any known technology generally used in ink production or toner production. The dispersing machine may be any of horizontal or vertical agitator mills, attritors, colloid mills, ball mills, three-roll mills, pearl mills, super mills, impellers, dispersers, KD mills, dynatrons, pressure kneaders. They are described in detail in *Latest Pigment Application Technology* (by CMC Publishing, 1986).

[0119]

The ink for inkjet of the invention may contain a surfactant, and the surfactant is described below.

The surfactant in the ink of the invention is effective for controlling the liquid properties of the ink, for improving the jet-out stability of the ink, for improving the waterproofness of the images formed of the ink, and for preventing ink bleeding on prints.

The surfactant includes anionic surfactants such as sodium dodecylsulfate, sodium dodecyloxysulfonate, sodium alkylbenzenesulfonate; cationic surfactants such as cetylpyridinium chloride, trimethylcetylammonium chloride, tetrabutylammonium chloride; and nonionic surfactants such as polyoxyethylene nonylphenyl ether,

polyoxyethylene naphthyl ether, polyoxyethylene octylphenyl ether. Especially preferred are nonionic surfactants.

[0120]

The surfactant content of the ink may be from 0.001 to 20 % by mass, preferably from 0.005 to 10 % by mass, more preferably from 0.01 to 5 % by mass.

[0121]

The ink for inkjet of the invention may be produced by dissolving or dispersing the above-mentioned dyes preferably along with a surfactant, in an aqueous medium. The "aqueous medium" as referred to herein is meant to indicate water or a mixture of water and a small amount of a water-miscible organic solvent, optionally containing additives such as moisturizer, stabilizer and preservative.

[0122]

In case where the dye is soluble in water, then it is preferably first dissolved in water in preparing the ink of the invention. Next, various solvent and additive are added to it, dissolved and mixed to give a uniform ink composition.

For dissolving the components, for example, various methods of stirring, ultrasonic irradiation or shaking may be employed. Especially preferred is a method of

stirring the components. When the components are stirred, various methods known in the art are employable. For example, they may be stirred in a mode of fluidization, reversed agitation, shear force stirring with dissolver, etc. Also preferably employed herein is a magnetic stirring method in which a magnetic stirrer is used for utilizing the shear force to the container bottom.

[0123]

Examples of the water-miscible organic solvent that may be used in the invention are alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, t-butanol, pentanol, hexanol, cyclohexanol, benzyl alcohol), polyalcohols (e.g., ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, butylene glycol, hexanediol, pentanediol, glycerin, hexanetriol, thiodiglycol), glycol derivatives (e.g., ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, triethylene glycol monomethyl ether, ethylene glycol diacetate, ethylene glycol monomethyl ether acetate, triethylene glycol

monomethyl ether, triethylene glycol monoethyl ether, ethylene glycol monophenyl ether), amines (e.g., ethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, morpholine, N-ethylmorpholine, ethylenediamine, diethylenetriamine, triethylenetetramine, polyethylenimine, tetramethylpropylenediamine), and other polar solvents (e.g., formamide, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, sulforane, 2-pyrrolidone, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 2-oxazolidone, 1,3-dimethyl-2-imidazolidinone, acetonitrile, acetone). Two or more of these water-miscible organic solvents may be used as combined.

[0124]

In case where the above-mentioned dyes are oil-soluble dyes, then they may be dissolved in a high-boiling-point organic solvent, and then emulsified and dispersed in an aqueous medium to prepare the ink of the invention.

The boiling point of the high-boiling-point organic solvent for use in the invention is 150°C or higher, but preferably 170°C or higher.

For example, the solvent includes phthalate (e.g., dibutyl phthalate, dioctyl phthalate, dicyclohexyl

phthalate, di-2-ethylhexyl phthalate, decyl phthalate,
 bis(2,4-di-tert-amylphenyl) isophthalate, bis(1,1-
 diethylpropyl) phthalate), phosphoric acid or phosphone
 esters (e.g., diphenyl phosphate, triphenyl phosphate,
 tricresyl phosphate, 2-ethylhexyldiphenyl phosphate,
 dioctylbutyl phosphate, tricyclohexyl phosphate, tri-2-
 ethylhexyl phosphate, tridecyl phosphate, di-2-
 ethylhexylphenyl phosphate), benzoates (e.g., 2-
 ethylhexyl benzoate, 2,4-dichlorobenzoate, dodecyl
 benzoate, 2-ethylhexyl p-hydroxybenzoate), amides (e.g.,
 N,N-diethyldodecanamide, N,N-diethylaurylamide),
 alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-
 tert-amylphenol), aliphatic esters (e.g., dibutoxyethyl
 succinate, di-2-ethylhexyl succinate, 2-hexyldecyl
 tetradecanoate, tributyl citrate, diethyl azelate,
 isostearyl lactate, trioctyl citrate), aniline
 derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-
 octylaniline), chloroparaffins (e.g., paraffins having a
 chlorine content of from 10 % to 80 %), trimesates (e.g.,
 tributyl trimesate), dodecylbenzene,
 diisopropylnaphthalene, phenols (e.g., 2,4-di-tert-
 amylphenol, 4-dodecyloxyphenol, 4-
 dodecyloxycarbonylphenol, 4-(4-
 dodecyloxyphenylsulfonyl)phenol), carboxylic acids (e.g.,
 2-(2,4-di-tert-amylphenoxybutyric acid, 2-ethoxyoctane-

decanoic acid), alkyl phosphates (e.g., di-2(ethylhexyl) phosphate, diphenyl phosphate). The amount of the high-boiling-point organic solvent to be used may be from 0.01 to 3 times, preferably from 0.01 to 1.0 time the oil-soluble dye in terms of the ratio by mass of the two.

The high-boiling-point organic solvents may be used either singly or as combined (for example, tricresyl phosphate and dibutyl phthalate; trioctyl phosphate and di(2-ethylhexyl) sebacate; dibutyl phthalate and poly(N-t-butylacrylamide)).

[0125]

Other examples than those mentioned hereinabove for the high-boiling-point organic solvent usable in the invention and/or methods for producing these high-boiling-point organic solvents are described, for example, in USP 2,322,027, 2,533,514, 2,772,163, 2,835,579, 3,594,171, 3,676,137, 3,689,271, 3,700,454, 3,748,141, 3,764,336, 3,765,897, 3,912,515, 3,936,303, 4,004,928, 4,080,209, 4,127,413, 4,193,802, 4,207,393, 4,220,711, 4,239,851, 4,278,757, 4,353,979, 4,363,873, 4,430,421, 4,430,422, 4,464,464, 4,483,918, 4,540,657, 4,684,606, 4,728,599, 4,745,049, 4,935,321, 5,013,639; EP 276,319A, 286,253A, 289,820A, 309,158A, 309,159A, 309,160A, 509,311A, 510,576A; East German Patents 147,009, 157,147, 159,573, 225,240A; British Patent 2,091,124A; JP-A 48-

47335, 50-26530, 51-25133, 51-26036, 51-27921, 51-27922, 51-149028, 52-46816, 53-1520, 53-1521, 53-15127, 53-146622, 54-91325, 54-106228, 54-118246, 55-59464, 56-64333, 56-81836, 59-204041, 61-84641, 62-118345, 62-247364, 63-167357, 63-214744, 63-301941, 64-9452, 64-9454, 64-68745, 1-101543, 1-102454, 2-792, 2-4239, 2-43541, 4-29237, 4-30165, 4-232946, 4-346338.

The amount of the high-boiling-point organic solvent to be used may be from 0.01 to 3.0 times, preferably from 0.01 to 1.0 time the oil-soluble dye in terms of the ratio by mass.

[0126]

In the invention, the oil-soluble dye and the high-boiling-point organic solvent are emulsified and dispersed in an aqueous medium. For their better emulsification, a low-boiling-point organic solvent may be used. The low-boiling-point organic solvent has a boiling point at normal pressure of from about 30°C to 150°C. Its preferred examples are esters (e.g., ethyl acetate, butyl acetate, ethyl propionate, β -ethoxyethyl acetate, methyl cellosolve acetate), alcohols (e.g., isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol), ketones (e.g., methyl isobutyl ketone, methyl ethyl ketone, cyclohexanone), amides (e.g., dimethylformamide, N-methylpyrrolidone), ethers (e.g., tetrahydrofuran,

dioxane), which, however, are not limitative.

[0127]

The emulsifying dispersion is as follows: A dye is dissolved in a high-boiling-point organic solvent alone, or its mixture with a low-boiling-point organic solvent to prepare an oil phase, and this is dispersed in an aqueous phase essentially comprising water to thereby form fine oily droplets of the oily phase. In this process, additives such as surfactant, moisturizer, dye stabilizer, emulsion stabilizer, preservative and antifungal described below may be added to any one or both of the aqueous phase and the oily phase, if desired.

For the emulsification, in general, the oily phase is added to the aqueous phase. Contrary to this, however, the aqueous phase may be dropwise added to the oily phase in a mode of phase-conversion emulsification. This is also preferable in the invention. When the dye for use in the invention is a water-soluble one and the additives are oil-soluble ones, then the emulsification method may also be employed.

[0128]

Various surfactants may be used in the emulsification. For example, preferred are anionic surfactants such as fatty acid salts, alkyl sulfate salts, alkylbenzenesulfonate salts, alkylnaphthalene sulfonate

salts, dialkylsulfosuccinate salts, alkylphosphate salts, naphthalenesulfonate-formalin condensates, polyoxyethylene alkylsulfate salts; and nonionic surfactants such as polyoxyethylene alkyl ethers, polyoxyethylene alkylallyl ethers, polyoxyethylene fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene alkylamines, glycerin fatty acid esters, oxyethylene-oxypropylene block copolymers. Also preferred are acetylene-based polyoxyethylene oxide surfactants, SURFYNOLS (by Air Products & Chemicals). Also preferred are amine oxide-type ampholytic surfactants such as N,N-dimethyl-N-alkylamine oxides. In addition, the surfactants described in JP-A 59-157636, pp. 37-38; and *Research Disclosure* No. 308119 (1989) are also usable herein.

[0129]

For stabilizing the emulsion immediately after its preparation, a water-soluble polymer may be added thereto along with the above-mentioned surfactant. Preferred examples of the water-soluble polymer are polyvinyl alcohol, polyvinylpyrrolidone, polyethylene oxide, polyacrylic acid, polyacrylamide and their copolymers. Also preferably used are natural water-soluble polymers such as polysaccharides, casein, gelatin. For stabilizing the dye dispersion, further usable are

polymers not substantially dissolving in aqueous media, for example, polyvinyl compounds, polyurethanes, polyesters, polyamides, polyureas, polycarbonates and others that are obtained through polymerization of acrylates, methacrylates, vinyl esters, acrylamides, methacrylamides, olefins, styrenes, vinyl ethers, acrylonitriles, etc. Preferably, these polymers have SO_3^- or COO^- . When such polymers not substantially dissolving in aqueous media are used herein, their amount is preferably at most 20 % by mass, more preferably at most 10 % by mass of the high-boiling-point organic solvent.

[0130]

When the oil-soluble dye and the high-boiling-point organic solvent are emulsified and dispersed to prepare aqueous ink, it is a matter of great importance to control the particle size of the dye dispersion. In order to increase the color purity and the density of the image formed in a mode of inkjet, it is indispensable to reduce the mean particle size of the dye particles in the inkjet ink. Preferably, the volume-average particle size of the dye particles is at most 1 μm , more preferably from 5 to 100 nm.

The volume-average particle size and the particle size distribution of the dispersed dye particles may be

readily determined in any known method. For it, for example, employable is a static light scattering method, a dynamic light scattering method, a centrifugal precipitation method, as well as the methods described in *Lecture of Experimental Chemistry*, 4th Ed., pp. 417-418. Concretely, an ink sample is diluted with distilled water to have a dye particle concentration of from 0.1 to 1 % by mass, and then analyzed with a commercially-available, volume-average particle sizer (e.g., Microtrack UPA, by Nikkiso) to readily determine the particle size of the dye particles. A dynamic light scattering method based on a laser Doppler effect is especially preferred for the measurement, in which even small particles can be measured.

The volume-average particle size is a mean particle size that is weighted by the volume of the particles. This is obtained by dividing the sum total of the products that are obtained by multiplying the diameter of each aggregated particle by the volume thereof, by the overall volume of all the particles. The volume-average particle size is described, for example, in S. Muroi, *Chemistry of Polymer Latex* (by Polymer Publishing), page 119.

[0131]

It has become obvious that coarse particles have a

significant influence on the printability of ink. Concretely, coarse particles clog heads, or even though not clogging, they soil heads and, as a result, ink could not be jetted out at all or is jetted unevenly. To that effect, coarse particles have a significant influence on the printability of ink. To evade the trouble, it is important that 1 μ l of ink contains at most 10 particles having a particle size of 5 μ m or more and at most 1000 particles having a particle size of 1 μ m or more.

To remove such coarse particles, for example, employable is any known centrifugation or precision filtration. The treatment for removing the coarse particles may be effected just after an emulsified dispersion for ink has been prepared, or after various additives such as moisturizer, surfactant and others have been added to the emulsified dispersion and just before the resulting ink is charged into an ink cartridge.

For effectively reducing the mean particle size and for removing coarse particles, employable is a mechanical emulsifier.

[0132]

The emulsifier may be any known one, including, for example, simple stirrers, impeller-assisted stirrers, in-line stirrers, mills such as colloid mills, ultrasonic stirrers. Above all, high-pressure homogenizers are

especially preferred.

The mechanism of high-pressure homogenizers is described in detail, for example, in USP 4,533,254 and JP-A 6-47264. Gaulin Homogenizer (by A.P.V. Gaulin), Microfluidizer (by Microfluidex) and Ultimizer (by Sugino Machine) are commercially available.

Recently, high-pressure homogenizers as in USP 5,720,551 have been developed, which are equipped with a mechanism of finely pulverizing particles in an ultra-high pressure jet flow, and these are preferred for the treatment of emulsification and dispersion in the invention. One example of the emulsifier with such an ultra-high pressure jet flow mechanism is DeBEE2000 (by Bee International).

[0133]

The pressure in emulsification in such a high-pressure emulsifying disperser is at least 50 MPa, preferably at least 60 MPa, more preferably at least 180 MPa.

Using at least two different types of emulsifiers is especially preferred in the invention. For example, the constituent components are first emulsified in a stirring emulsifier and then further emulsified in a high-pressure homogenizer. Also preferred is a method that comprises once emulsifying and dispersing the constituent

components in the emulsifier as above, then adding additives such as moisturizer, surfactant and others to the resulting emulsion, and further emulsifying it in a high-pressure homogenizer before the resulting ink is charged into a cartridge.

In case where a low-boiling-point organic solvent is used along with the high-boiling-point organic solvent as above, it is desirable to remove the low-boiling-point solvent from the emulsion for ensuring the stability, the safety and the sanitation of the emulsion. For removing the low-boiling-point solvent, various methods may be employed depending on the type of the solvent to be removed. For example, employable is evaporation, vacuum evaporation or ultrafiltration. It is desirable that the low-boiling-point organic solvent is removed as soon as possible immediately after the preparation of the emulsion.

[0134]

Methods of preparing inkjet ink are described in detail, for example, in JP-A 5-148436, 5-295312, 7-97541, 7-82515, 7-118584, and the description may apply to the preparation of the ink for inkjet recording of the invention.

[0135]

In preparing the ink for inkjet of the invention,

ultrasonic waves may be given to the system where dyes and additives are dissolved in a medium.

The ultrasonic vibration in the ink preparation is for removing bubbles from the ink. This is because, when ink receives pressure from a recording head, then it may produce bubbles. To prevent this, ultrasonic energy which is equal to or higher than the energy that the ink may receive from a recording head is previously applied to the ink so as to remove the bubbles.

The ultrasonic vibration is generally at a frequency of at least 20 kHz, preferably at least 40 kHz, more preferably at least 50 kHz. The energy to be applied to the ink by the ultrasonic vibration is generally at least 2×10^7 J/m³, preferably at least 5×10^7 J/m³, more preferably at least 1×10^8 J/m³. The time for the ultrasonic vibration is generally from 10 minutes to 1 hour or so.

[0136]

The ultrasonic vibration may be effectively attained at anytime after the dye has been put into a medium. After the finished ink has been once stored, it may be exposed to ultrasonic waves, and this is also effective. However, it is more desirable that ultrasonic waves are applied to the dye while the dye is dissolved and/or dispersed in a medium, since their effect to remove bubbles is larger and since they promote the dissolution

and/or dispersion of the dye in the medium.

Accordingly, at least the ultrasonic treatment may be effected in any stage while or after the dye is dissolved and/or dispersed in a medium. In other words, the ultrasonic treatment may be effected at least once at anytime after the ink has been prepared and before it is finished to be a commercial product.

[0137]

In one preferred embodiment of the invention, the process of dissolving and/or dispersing the dye in a medium comprises a step of dissolving it in a part of a medium and a step of mixing the remaining medium with the resulting dye solution. Preferably, ultrasonic waves are applied to the system in at least any one of these steps. More preferably, at least ultrasonic waves are applied to the system in the former step of dissolving the dye in a part of a medium.

The latter step of mixing the remaining medium with the resulting dye solution may be effected in one stage or in plural stages.

[0138]

In preparing the ink of the invention, it is desirable that the system is degassed under heat or under reduced pressure. This is preferable for more effectively removing bubbles from the ink. The step of

degassing the system under heat or under reduced pressure is preferably effected simultaneously with or after the step of mixing the remaining medium with the previously-prepared dye solution.

Ultrasonic waves to be applied to the system of ink preparation may be generated by the use of any known ultrasonicator.

[0139]

In preparing the ink for inkjet of the invention, it is also important to filter the prepared ink composition so as to remove impurities from it. In this treatment, a filter is used. The filter has an effective pore size of at most 1 μm , preferably from 0.05 μm to 0.3 μm , more preferably from 0.25 μm to 0.3 μm . Various materials may be used for forming the filter. Especially for the ink of water-soluble dye, the filter is preferably one that is specifically designed for aqueous solvents. More preferably, the filter is formed of a polymer material that may well trap impurities. For the filtration, the ink composition may be passed through the filter in a mode of ordinary liquid feeding. Apart from it, any other mode of pressure filtration or reduced pressure filtration may also be employed herein.

[0140]

After the filtration, the ink may often take air

therein. Bubbles from the air may often cause disturbed images in inkjet recording. Therefore, it is desirable that the ink is further processed for additional degassing as in the above. For degassing it, for example, the ink may be kept static for a while after filtered, or it may be degassed ultrasonically or under reduced pressure by the use of commercially-available devices. Preferably, the ultrasonic degassing is effected for 30 seconds to 2 hours, more preferably for 5 minutes to 1 hour or so.

[0141]

These treatments are preferably effected in a space of clean room or clean bench in order to prevent the ink from being contaminated with impurities during the treatments. In the invention, it is desirable that the treatments are effected in a space having a degree of cleanness of at most class 1000. The "degree of cleanness" indicates the value measured with a dust counter.

[0142]

The ink for inkjet of the invention may contain a drying inhibitor for preventing the ink from being clogged by drying at the inkjet nozzle orifice, a penetration promoter for promoting the penetration of the ink into paper, and other various additives such as UV

absorbent, antioxidant, viscosity improver, surface tension improver, dispersant, dispersion stabilizer, antifungal, rust-proofing agent, pH-controlling agent, defoaming agent, chelating agent. The ink of the invention may contain any of these suitably selected for it.

[0143]

For the drying inhibitor used in the invention, preferred is a water-soluble organic solvent having a lower vapor pressure than water. Its concrete examples are polyalcohols such as typically ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, thiodiglycol, dithiodiglycol, 2-methyl-1,3-propanediol, 1,2,6-hexanetriol, acetylene glycol derivatives, glycerin, trimethylolpropane; polyalcohol lower alkyl ethers such as ethylene glycol monomethyl (or ethyl) ether, diethylene glycol monomethyl (or ethyl) ether, triethylene glycol monoethyl (or butyl) ether; heterocyclic compounds such as 2-pyrrolidone, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, N-ethylmorpholine; sulfur-containing compounds such as sulforane, dimethyl sulfoxide, 3-sulforene; polyfunctional compounds such as diacetone alcohol, diethanolamine; and urea derivatives. Of those, more preferred are polyalcohols such as glycerin and

diethylene glycol. these drying inhibitors may be used either singly or two or more as combined. Preferably, the drying inhibitor content of the ink is from 10 to 50 % by mass.

[0144]

For the penetration promoter used in the invention, for example, herein usable are alcohols such as ethanol, isopropanol, butanol, di(tri)ethylene glycol monobutyl ether, 1,2-hexanediol; and sodium laurylsulfate, sodium oleate, or nonionic surfactants. In general, the penetration promoter is enough when its amount in the ink is from 10 to 30 % by mass. However, its amount is preferably so controlled that the ink does not cause bleeding and print-through.

[0145]

The UV absorbent is for improving the image stability in the invention. For the UV absorbent, herein usable are benzotriazole compounds as in JP-A 58-185677, 61-190537, 2-782, 5-197075, 9-34057; benzophenone compounds as in JP-A 46-2784, 5-194483, and USP 3,214,463; cinnamate compounds as in JP-B 48-30492, 56-21141, and JP-A 10-88106; triazine compounds as in JP-A 4-298503, 8-53427, 8-239368, 10-182621, and JP-T 8-501291 (the term "JP-T" as used herein means a published Japanese translation of a PCT patent application);

compounds as in *Research Disclosure* No. 24239; and other compounds capable of absorbing UV rays to emit fluorescence, or that is, fluorescent brighteners such as typically stilbene compounds and benzoxazole compounds.

[0146]

The antioxidant is for improving the image stability in the invention. For it, herein usable are various organic or metal complex-type fading inhibitors. The organic fading inhibitors include hydroquinones, alkoxyphenols, dialkoxyphenols, phenols, anilines, amines, indanes, chromans, alkoxyanilines, and heterocyclic compounds; and the metal complexes include nickel complexes and zinc complexes. More concretely, herein usable are the compounds described in the patent publications that are referred to in *Research Disclosure* No. 17643, Items VII-I to J, No. 15162, No. 18716, page 650, left column, No. 36544, page 527, No. 307105, page 872, and No. 15162, as well as the compounds that fall within the range of the general formula to indicate the typical compounds and the examples of the compounds described in pp. 127-137 of JP-A 62-215272.

[0147]

The antifungal agent used in the invention includes sodium dehydroacetate, sodium benzoate, sodium pyridinethione-1-oxide, ethyl p-hydroxybenzoate, 1,2-

benzothiazolin-3-one and its salts. Preferably, its amount in the ink is from 0.02 to 5.00 % by mass.

Its details are described in, for example, *Dictionary of Antibacterials and Antifungals* (by the Dictionary Section of the Antibacterial and Antifungal Society of Japan).

The rust-proofing agent includes, for example, acidic sulfites, sodium thiosulfate, ammonium thioglycolate, diisopropylammonium nitrite, pentaerythritol tetranitrate, dicyclohexylammonium nitrite, benzotriazole. Preferably, its amount in the ink is from 0.02 to 5.00 % by mass.

[0148]

The pH-controlling agent used in the invention is preferably used for pH control and for dispersion stabilization. Preferably, the pH of the ink is controlled to fall between 8 and 11 at 25°C. If the pH is lower than 8, then the dye solubility will lower and nozzles will be readily clogged. However, if the pH is higher than 11, the waterproofness of the ink will be poor. The pH-controlling agent may be a basic compound such as organic bases and inorganic alkalis, or an acidic compound such as organic acids and inorganic acids.

The basic compound includes, for example, sodium hydroxide, potassium hydroxide, sodium carbonate,

potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, sodium acetate, potassium acetate, sodium phosphate, sodium monohydrogen phosphate and other inorganic compounds, as well as aqueous ammonia, methylamine, ethylamine, diethylamine, triethylamine, ethanolamine, diethanolamine, triethanolamine, ethylenediamine, piperidine, diazabicyclooctane, diazabicycloundecene, pyridine, quinoline, picoline, lutidine, collidine and other organic bases.

The acidic compound includes, for example, inorganic compounds such as hydrochloric acid, sulfuric acid, phosphoric acid, boric acid, sodium hydrogensulfate, potassium hydrogensulfate, potassium dihydrogenphosphate, sodium dihydrogenphosphate; and organic compounds such as acetic acid, tartaric acid, benzoic acid, trifluoroacetic acid, methanesulfonic acid, ethanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, saccharinic acid, phthalic acid, picolinic acid, quinolinic acid.

[0149]

The conductivity of the ink of the invention may fall between 0.01 and 10 S/m, preferably between 0.05 and 5 S/m.

The conductivity may be measured according to an electrode method using a commercially-available saturated potassium chloride.

The conductivity may be controlled essentially by the ion concentration of the aqueous solution. When the salt concentration thereof is high, the solution may be de-salted through ultrafiltration. When a salt or the like is added to control the conductivity of the solution, various organic salts or inorganic salts may be used for the purpose.

The inorganic salts are, for example, inorganic compounds such as potassium halides, sodium halides, sodium sulfate, potassium sulfate, sodium hydrogensulfate, potassium hydrogensulfate, sodium nitrate, potassium nitrate, sodium hydrogencarbonate, potassium hydrogencarbonate, sodium phosphate, sodium monohydrogenphosphate, borates, potassium dihydrogenphosphate, sodium dihydrogenphosphate; and organic compounds such as sodium acetate, potassium acetate, potassium tartrate, sodium tartrate, sodium benzoate, potassium benzoate, sodium p-toluenesulfonate, potassium saccharinate, potassium phthalate, sodium picolinate.

The conductivity of the ink may also be controlled by specifically selecting the components of the other additives.

[0150]

The viscosity of the ink of the invention may be

from 1 to 20 mPa·s at 25°C, but is preferably from 2 to 15 mPa·s, more preferably from 2 to 10 mPa·s. If the viscosity is higher than 30 mPa·s, the fixation of the recorded image may be retarded and the ink jet-out potency may lower. If the viscosity is lower than 1 mPa·s, the recorded image may be blurred and its quality is therefore lowered.

The viscosity may be controlled in any desired manner by controlling the amount of the ink solvent. The ink solvent includes, for example, glycerin, diethylene glycol, triethanolamine, 2-pyrrolidone, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether.

If desired, a viscosity improver may be used. The viscosity improver includes, for example, celluloses, water soluble polymers such as polyvinyl alcohol, and nonionic surfactants. Its details are described in, for example, *Viscosity Control Technology* (by the Technology Information Association, 1999), Chap. 9; *Chemicals for Inkjet Printers* (extra ed., '98) - Investigation of Trends and Views in Development of Materials (by CMC, 1997), pp. 162-174.

[0151]

Methods of measuring the viscosity of liquid are described in detail in JIS Z8803. In the invention, the viscosity of the ink may be readily measured in a simple

manner by the use of commercially-available viscometers. For example, there are known Tokyo Instrument's rotary viscometers, B-type Viscometer and E-type Viscometer. In the invention, Yamaichi Electric's shaking viscometer, VM-100A-L Model was used to measure the viscosity at 25°C. The viscosity unit is Pascal-second (Pa·s), but generally milli-Pascal-second (mPa·s).

[0152]

Preferably, the surface tension of the ink of the invention is from 20 to 50 mN/m at 25°C, both in terms of the dynamic surface tension and the static surface tension. More preferably, it is from 20 to 40 mN/m. If the surface tension is higher than 50 mN/m, then the jet-out stability of the ink will be poor. If so, in addition, the print formed through multi-color superimposition will be blurred and whiskered and the print quality will be significantly lowered. On the other hand, if the surface tension thereof is 20 mN/m or less, the ink may adhere to the surfaces of printer tools to worsen the print quality.

For controlling the surface tension of the ink, various cationic, anionic or nonionic surfactants such as those mentioned hereinabove may be added to the ink for inkjet. Preferably, the amount of the surfactant that may be in the ink is from 0.01 to 20 % by mass, more

preferably from 0.1 to 10 % by mass. If desired, two or more different types of surfactants may be combined for use in the ink.

[0153]

For measuring the static surface tension of ink, known are a capillary ascending method, a dropping method, and a ring hanging method. In the invention, the static surface tension of the ink is measured according to a vertical plate method.

Briefly, when a thin plate of glass or platinum is hung vertically while a part of it is dipped in a liquid, then the surface tension of the liquid acts in the downward direction along the part at which the liquid is in contact with the plate. The force of surface tension is balanced with a force acting in the upward direction to thereby determine the surface tension of the liquid.

[0154]

For measuring the dynamic surface tension of ink, known are a vibration jetting method, a meniscus dropping method, and a maximum bubble pressure method, for example, as in *Lecture of New Experimental Chemistry*, Vol. 18, "Interface and Colloid" (by Maruzen), pp. 69-90 (1977). Also known is a liquid membrane breaking method, for example, as in JP-A 3-2064. In the invention, the dynamic surface tension of the ink is measured according

to a bubble pressure differential method. The principle and the mechanism of the method are described below.

[0155]

When an uniform solution prepared by stirring is bubbled, then new vapor-liquid interfaces are formed, and surfactant molecules in the solution gather around the surface of water at a constant rate. In that condition, the bubble rate (bubble-forming rate) is varied. When the bubble rate is slow, then a larger number of surfactant molecules gather around the surfaces of the bubbles formed, and the maximum bubble pressure just before the bubbles crack is low. The maximum bubble pressure (surface tension) to the bubble rate is detected. One preferred embodiment of measuring the dynamic surface tension of the ink is as follows: One large probe and one small probe, totaling two, are used, and bubbles are formed in the solution. In the maximum bubble pressure condition of the two probes, the differential pressure is measured, and the dynamic surface tension of the ink is calculated from it.

[0156]

Preferably, the nonvolatile content of the ink of the invention is from 10 to 70 % by mass of the ink for ensuring the jet-out stability of the ink and ensuring the good print quality thereof in point of the image

fastness, the image blurring resistance and the non-stickiness of the printed matter. More preferably, it is from 20 to 60 % by mass for more favorably ensuring the jet-out stability of the ink and ensuring the good print quality thereof especially in point of the image blurring resistance of the printed matter.

The nonvolatile content includes liquid and solid components and polymer components having a boiling point not lower than 150°C under one atmosphere. The nonvolatile components of ink for inkjet recording are dye, high-boiling-point solvent, and other optional polymer latex, surfactant, dye stabilizer, antifungal and buffer. Most of these nonvolatile components except dye stabilizer lower the dispersion stability of ink, and remain on the printed image-receiving paper for inkjet to interfere with dye association and stabilization thereon, and, as a result, the image fastness is thereby worsened and the printed image is often blurred under high-humidity condition.

[0157]

The ink of the invention may contain a polymer compound. The polymer compound is meant to indicate any and every polymer compound having a number-average molecular weight of at least 5000 in the ink. The polymer compound includes water-soluble polymer compounds

that are substantially soluble in aqueous media, water-dispersible polymer compounds such as polymer latex and polymer emulsion, as well as alcohol-soluble polymer compounds that are soluble in polyalcohols serving as auxiliary solvent. So far as they substantially uniformly dissolve or disperse in ink, any polymer compounds may be in the ink of the invention.

[0158]

Examples of the water-soluble polymer compounds are polyvinyl alcohol, silanol-modified polyvinyl alcohol, carboxymethyl cellulose, hydroxyethyl cellulose, polyvinylpyrrolidone, polyalkylene oxides such as polyethylene oxide, polypropylene oxide, polyalkylene oxide derivatives and other water-soluble polymers; as well as natural water-soluble polymers such as polysaccharides, starch, cationated starch, casein, gelatin; aqueous acrylic resins such as polyacrylic acid, polyacrylamide and their copolymers; aqueous alkyd resins, and other water-soluble polymer compounds having -SO_3^- or -COO^- in the molecule and substantially soluble in aqueous media.

The polymer latex includes, for example, styrene-butadiene latex, styrene-acryl latex, polyurethane latex. The polymer emulsion is acrylic emulsion, etc.

These water-soluble polymer compounds may be used

either singly or two or more as combined.

[0159]

The water-soluble polymer compound is used as a viscosity improver, as so mentioned hereinabove, for controlling the ink viscosity to fall within a suitable viscosity region for ensuring good jet-out potency of the ink. However, if the ink contains the compound too much, then the ink viscosity may increase and the jet-out stability of the ink will be poor. If so, in addition, the ink may form precipitates when elapsed, and may therefore clog nozzles.

The amount of the polymer compound to be added to the ink for viscosity control may be from 0 to 5 % by mass of the ink, though depending on the molecular weight of the compound (the amount of the compound having a higher molecular weight may be smaller). Preferably, it is from 0 to 3 % by mass, more preferably from 0 to 1 % by mass.

Apart from the surfactants mentioned above, other various nonionic, cationic or anionic surfactants may also be included as surface tension improver. For example, the anionic surfactants are fatty acid salts, alkyl sulfate salts, alkylbenzenesulfonate salts, alkylnaphthalene sulfonate salts, dialkylsulfosuccinate salts, alkylphosphate salts, naphthalenesulfonate-

formalin condensates, polyoxyethylene alkylsulfate salts. The nonionic surfactants are polyoxyethylene alkyl ethers, polyoxyethylene alkylaryl ethers, polyoxyethylene fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene alkylamines, glycerin fatty acid esters, oxyethylene-oxypropylene block copolymers. Also preferred are acetylene-based polyoxyethylene oxide surfactants, SURFYNOLS (by Air Products & Chemicals). Also preferred are amine oxide-type ampholytic surfactants such as N,N-dimethyl-N-alkylamine oxides. In addition, the surfactants described in JP-A 59-157636, pp. 37-38; and *Research Disclosure* No. 308119 (1989) are also usable herein.

[0160]

In the invention, various cationic, anionic and nonionic surfactants such as those mentioned hereinabove may be used as a dispersant and a dispersion stabilizer, and fluorine-containing compounds, silicone compounds and chelating agents such as EDTA may be used as a defoaming agent, if desired.

[Examples]

[0161]

The invention is described with reference to the following Examples, to which, however, the invention should not be limited.

(Example 1)

Ultrapure water (resistance, at least 18 MΩ) was added to the following components shown below to make one liter, and then stirred under heat at 30 to 40°C for 1 hour. Next, the resulting mixture was filtered under reduced pressure through a micro-filter having a mean pore size of 0.25 μm. Inks of different colors were thus prepared.

[Formulation of Light Cyan Ink]

(Solid Components)

Cyan Dye (C-1)	20 g/liter
Urea (UR)	15 g/liter
Benzotriazole (BTZ)	0.08 g/liter
Proxel XL2 (PXL)	3.5 g/liter

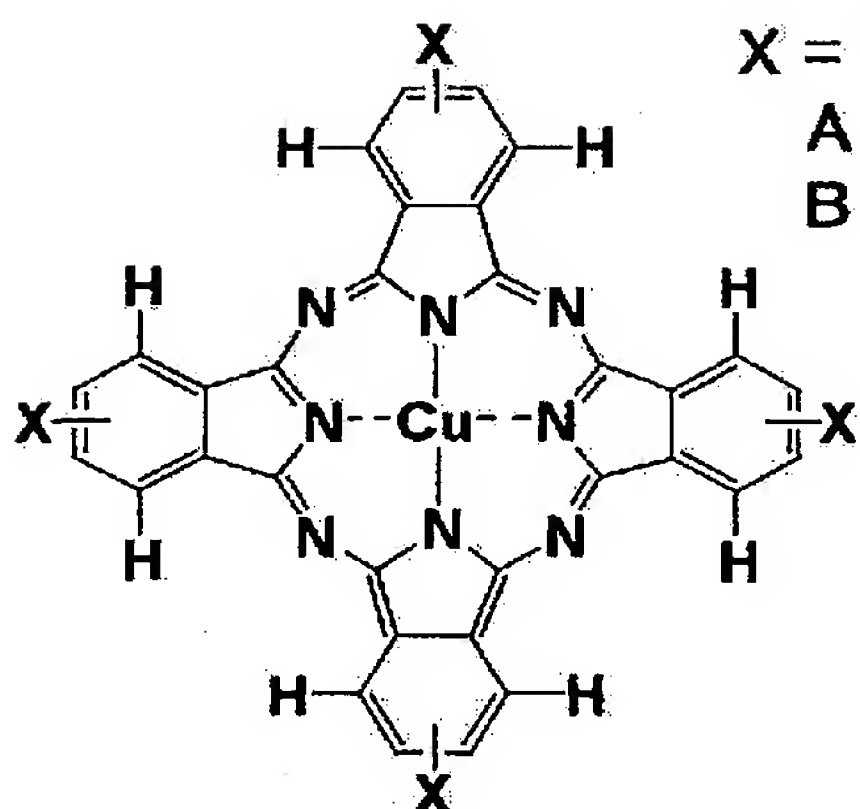
(Liquid Components)

Triethylene Glycol (TEG)	110 g/liter
Glycerin (GR)	130 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	110 g/liter
2-Pyrrolidone (PRD)	60 g/liter
Triethanolamine (TEA)	7 g/liter
Surfynol STG (SW)	10 g/liter

[0162]

Cyan Dye (C-1):

[chem.14]



X = A or B

A : $\text{SO}_2(\text{CH}_2)_3\text{SO}_3\text{Li}$

B : $\text{SO}_2(\text{CH}_2)_3\text{SO}_2\text{NHCH}_2\text{CH}(\text{CH}_3)\text{OH}$

C-1 : A/B = 75/25

[0163]

[Formulation of Cyan Ink]

(Solid Components)

Cyan Dye (C-1)	60 g/liter
Urea (UR)	30 g/liter
Benzotriazole (BTZ)	0.08 g/liter
Proxel XL2 (PXL)	3.5 g/liter
(Liquid Components)	
Triethylene Glycol (TEG)	110 g/liter
Glycerin (GR)	130 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	130 g/liter
2-Pyrrolidone (PRD)	60 g/liter
Triethanolamine (TEA)	7 g/liter
Surfynol STG (SW)	10 g/liter

[0164]

(Formulation of Light Magenta Ink)

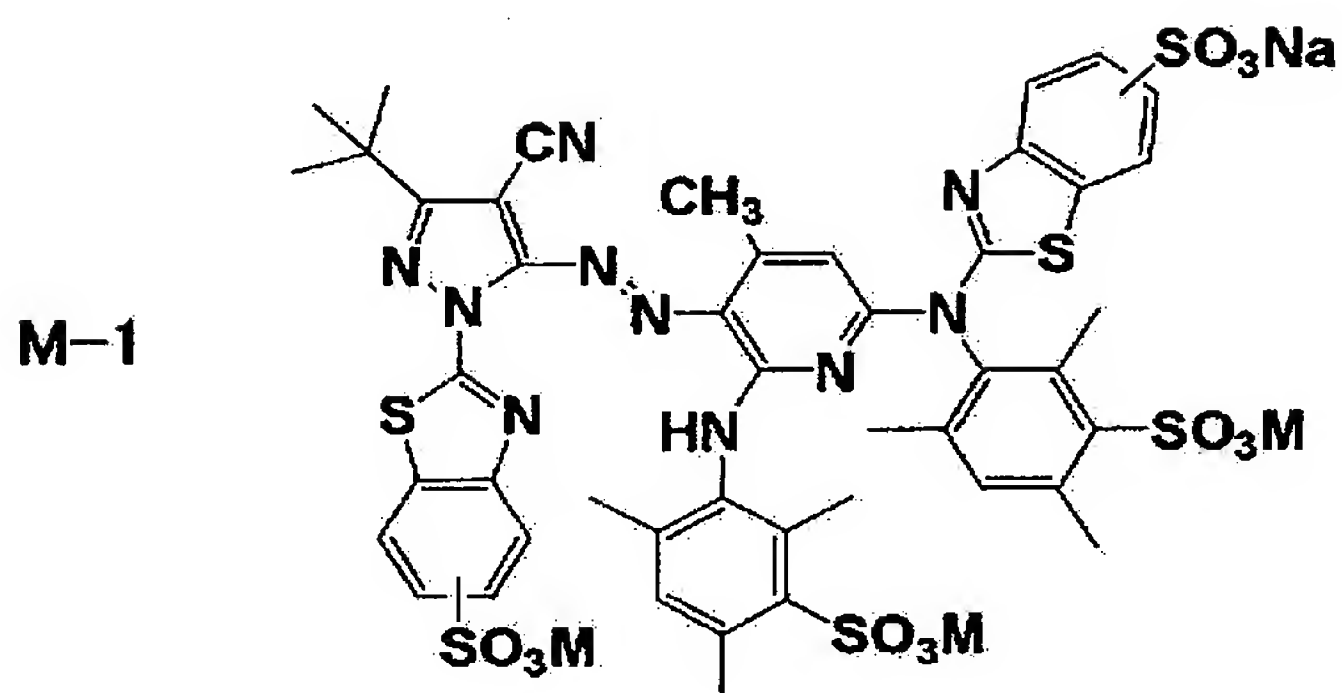
(Solid Components)

Magenta Dye (M-1)	7.5 g/liter
Urea (UR)	10 g/liter
Proxel	5 g/liter
(Liquid Components)	
Diethylene Glycol (DEG)	90 g/liter
Glycerin (GR)	70 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	70 g/liter
Triethanolamine (TEA)	6.9 g/liter
Surfynol STG (SW)	10 g/liter

[0165]

Magenta Dye (M-1):

[chem.15]



[0166]

(Formulation of Magenta Ink)

(Solid Components)

Magenta Dye (M-1)	23 g/liter
Urea (UR)	15 g/liter
Proxel	5 g/liter

(Liquid Components)

Diethylene Glycol	90 g/liter
Glycerin	70 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	
	70 g/liter
Triethanolamine	6.9 g/liter
Surfynol STG	10 g/liter

[0167]

(Formulation of Yellow Ink)

(Solid Components)

Yellow Dye (Y-1)	35 g/liter
Proxel	3.5 g/liter
Benzotriazole (BTZ)	0.08 g/liter
Urea	10 g/liter

(Liquid Components)

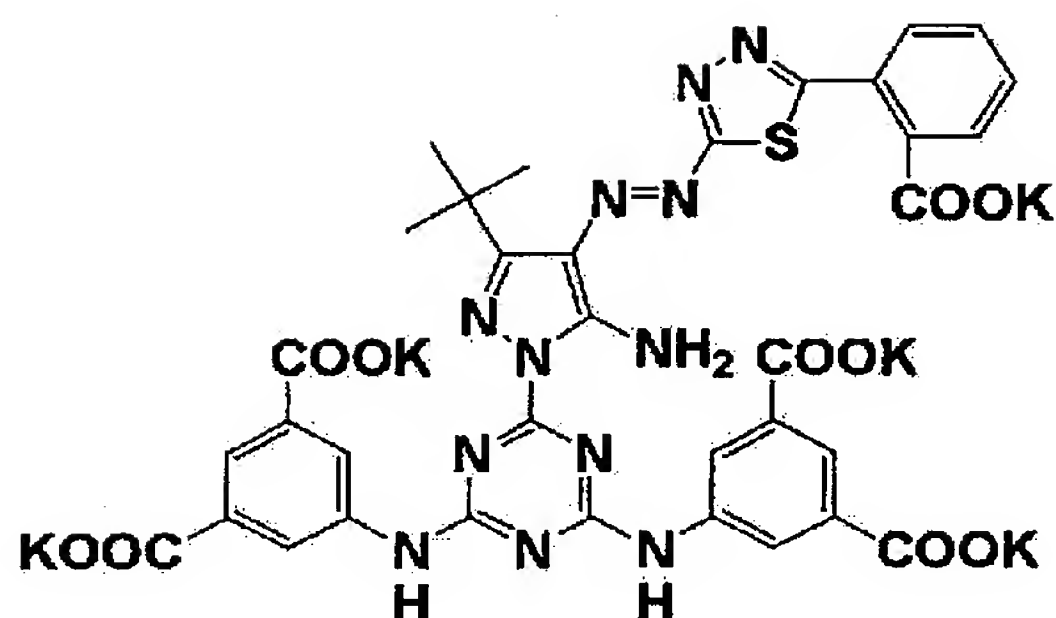
Triethylene Glycol Monobutyl Ether (TGB)	
	130 g/liter
Glycerin (GR)	115 g/liter
Diethylene Glycol (DEG)	120 g/liter
2-Pyrrolidone	35 g/liter
Triethanolamine (TEA)	8 g/liter
Surfynol STG (SW)	10 g/liter

[0168]

Yellow Dye (Y-1):

[chem.16]

Y-1



[0169]

(Formulation of Dark Yellow Ink)

(Solid Components)

Yellow Dye (Y-1)	35 g/liter
Magenta Dye (M-1)	2 g/liter
Cyan Dye (C-1)	2 g/liter
Proxel	5 g/liter
Benzotriazole (BTZ)	0.08 g/liter
Urea	10 g/liter

(Liquid Components)

Triethylene Glycol Monobutyl Ether (TGB)	140 g/liter
Glycerin (GR)	125 g/liter
Diethylene Glycol (DEG)	120 g/liter
2-Pyrrolidone	35 g/liter
Triethanolamine (TEA)	8 g/liter
Surfynol STG (SW)	10 g/liter

[0170]

(Formulation of Black Ink)

(Solid Components)

Black Dye (BK-1) [λ_{max} , 587 nm; half-value width, 105 nm]

75 g/liter

Black Dye (BK-2) [λ_{max} , 447 nm] 30 g/liter

Proxel 5 g/liter

Urea 10 g/liter

Benzotriazole 3 g/liter

(Liquid Components)

Diethylene Glycol Monobutyl Ether (DGB)

120 g/liter

Glycerin (GR) 125 g/liter

Diethylene Glycol (DEG) 100 g/liter

2-Pyrrolidone 35 g/liter

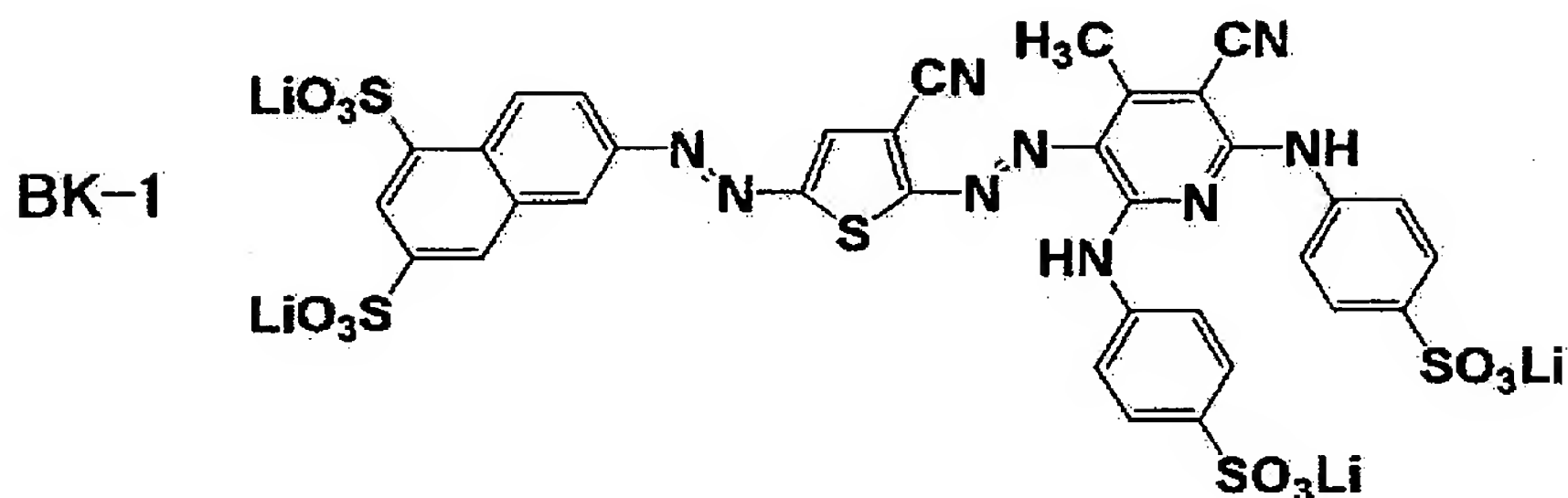
Triethanolamine (TEA) 8 g/liter

Surfynol STG (SW) 10 g/liter

[0171]

Black Dye (BK-1):

[chem.17]

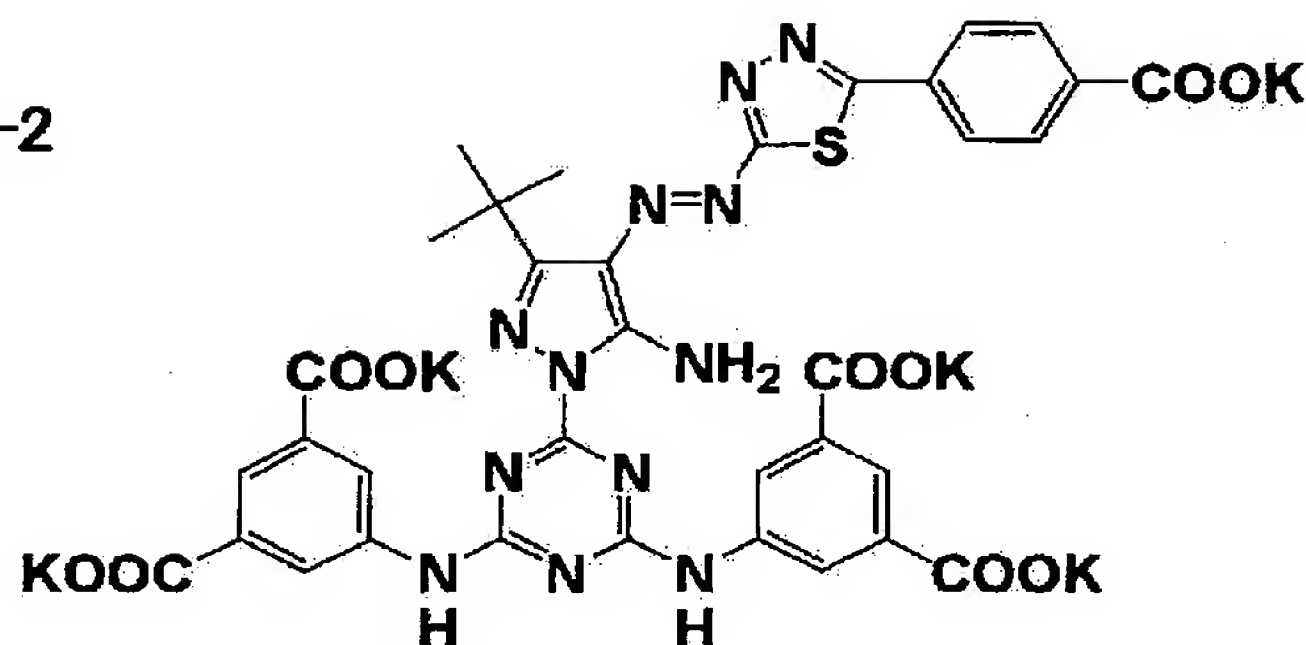


[0172]

Black Dye (BK-2):

[chem.18]

BK-2



[0173]

An ink set of these inks was prepared, and this is IS-101. In addition, other ink sets IS-102 to IS-108 were prepared in the same manner as above, in which, however, the dye of the black ink was partly changed as in the following Table.

The dyes used herein all had a positive oxidation potential (E_{ox}) over 1.2 V (vs SCE).

[0174]

[Table 1]

	Additive
IS-101 (comparison)	no
IS-102 (comparison)	A half of BK-1 in IS-101 was changed to dye A.
IS-103 (comparison)	A half of BK-1 in IS-101 was changed to dye B.
IS-104 (the invention)	A half of BK-1 in IS-101 was changed to dye C.
IS-105 (the invention)	A half of BK-1 in IS-101 was changed to dye D.
IS-106 (the invention)	1/3 of BK-1 in IS-101 was changed to dye C.
IS-107 (the invention)	1/3 of BK-1 in IS-101 was changed to dye D.
IS-108 (the invention)	A half of BK-1 in IS-101 was changed to dye E.

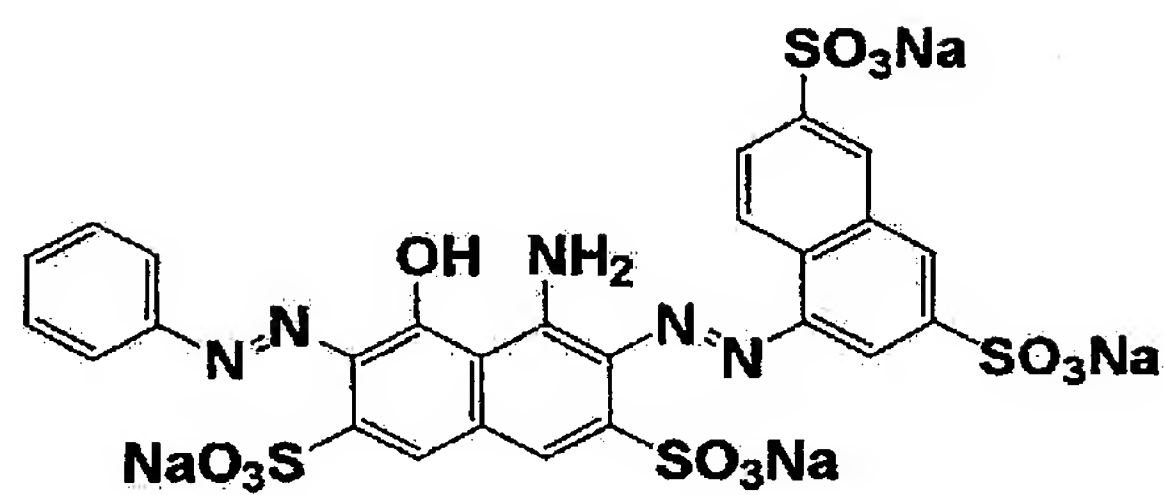
[0175]

[chem.19]

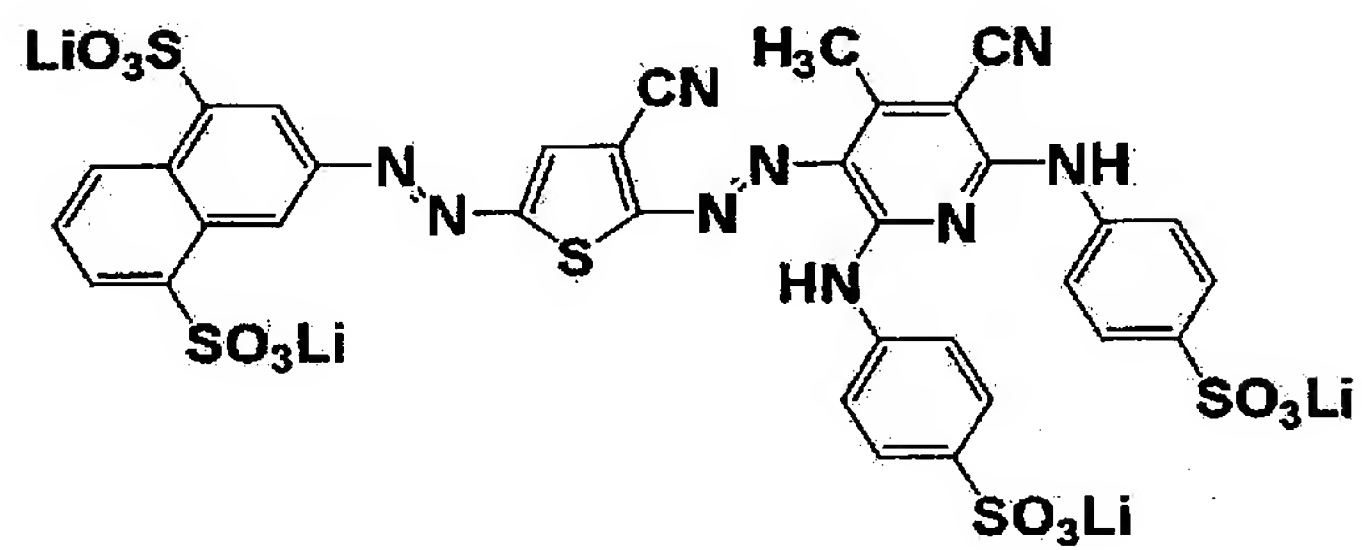
Dye A

C.I.Direct Black 38

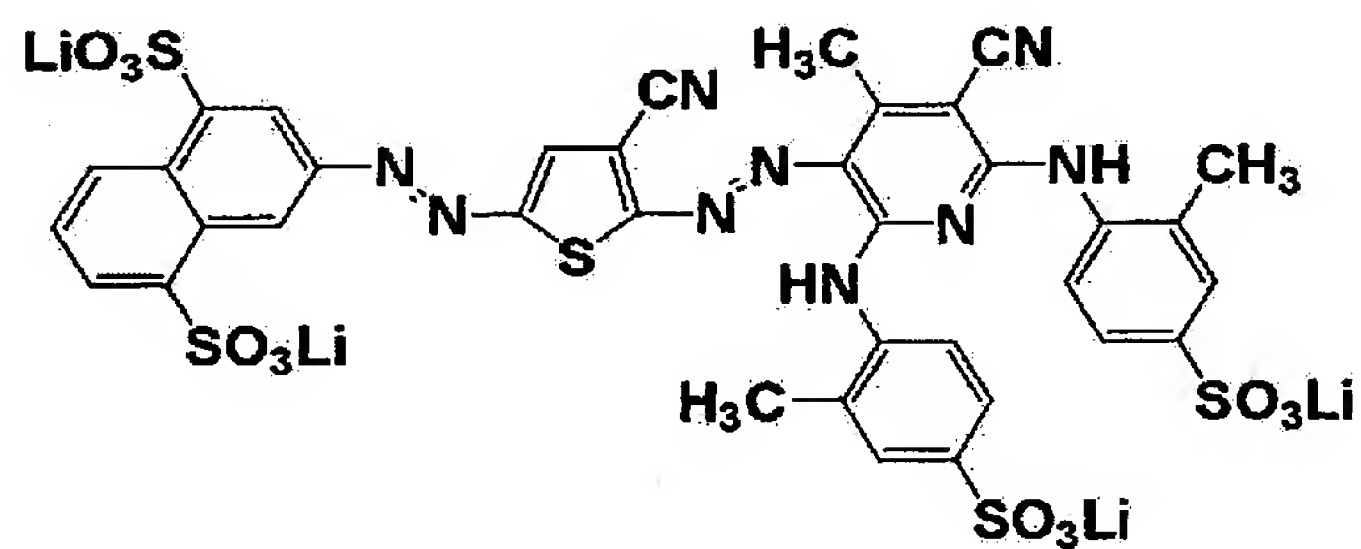
Dye B



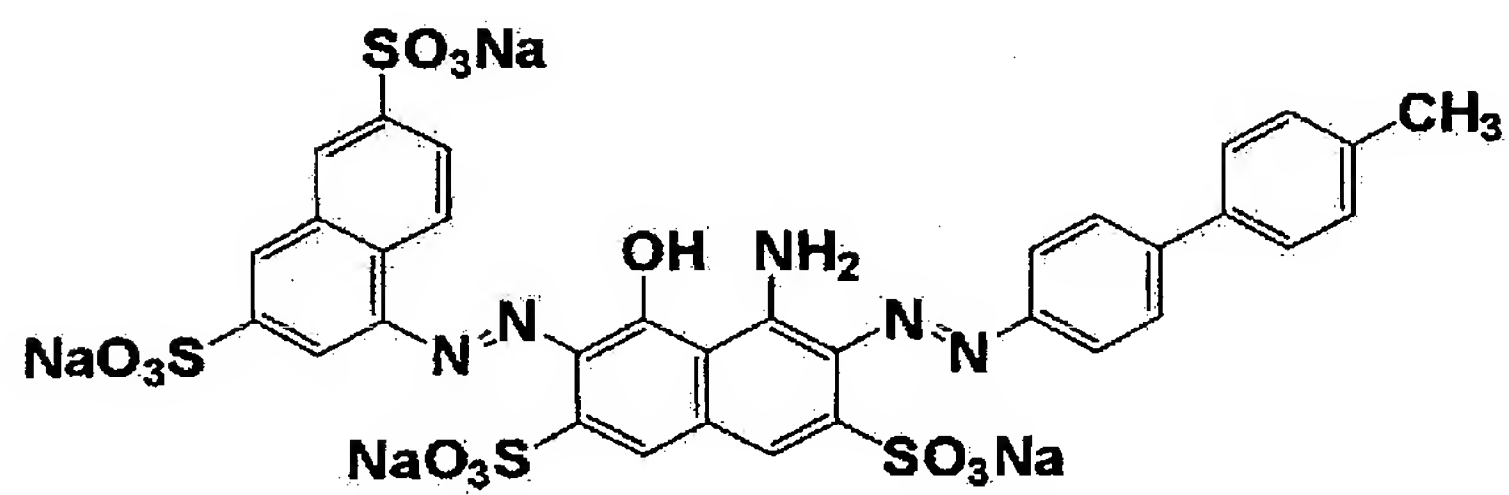
Dye C



Dye D



Dye E



[0176]

These inks were charged in ink cartridges of EPSON's inkjet printer PM-980C, and the printer was driven in a mode of monochromatic image formation to thereby print a stepwise density-varying gray image pattern on an image-receiving sheet.

The image-receiving sheet used herein is Fuji Photo Film's inkjet paper, photo-glossy paper "Gasai".

[0177]

(Evaluation Tests)

1) Using a densitometer, X-RITE, a value of Dvis of each sample is measured, and this indicates the maximum gray density.

2) The image storability of the gradation gray image is evaluated, as follows:

1. The light fastness is evaluated as follows: The image density C_i of the fresh sample just after printed is measured with X-RITE 310. Then, the printed image is exposed to xenon light (85,000 lux) from Atlas' weather meter for 20 days, and then its image density C_f is measured. The dye retentiveness is obtained from $\{(C_f/C_i) \times 100\}$, and this indicates the light fastness of the printed sample. Regarding the dye retentiveness, three points having a reflection density of 1, 1.5 and 2 are analyzed in every sample. The samples having a dye retentiveness of at least 80 % at every point are "A";

those having a dye retentiveness of less than 80 % at two points are "B"; and those having a dye retentiveness of less than 80 % at all three points are "C".

2. The ozone resistance is evaluated as follows: photo-glossy paper on which image is formed are kept in a box having a constant ozone gas concentration of 5 ppm, for 7 days. Before and after exposure to ozone gas, the image density of each sample is measured with a reflection densitometer (X-Rite 310TR), and the dye retentiveness in every sample is determined. Regarding the dye retentiveness, three points having a reflection density of 1, 1.5 and 2.0 are analyzed in every sample. The ozone gas concentration in the box is kept constant by the use of an ozone gas monitor (Applics' Model OZG-EM-01).

Thus tested, the samples are grouped into three ranks: Those having a dye retentiveness of at least 80 % at every point are "A"; those having a dye retentiveness of less than 80 % at one or two points are "B"; and those having a dye retentiveness of less than 80 % at all three points are "C".

3. The ink jet-out stability is evaluated as follows: Under a controlled condition at 30°C and 80 % RH, 100 sheets of A4-size paper are printed with each ink set. The printed black images are checked for image disorder

and thin spots. The samples with no trouble are A; those having some image disorder and other trouble are B; and those having many troubles are C.

[0178]

[Table 2]

	Maximum Density	Light Fastness	Ozone Resistance	Ink Jet-Out Stability
PM-980C (comparison)	2.43	C	C	A
IS-101 (comparison)	2.21	A	A	C
IS-102 (comparison)	2.31	B	B	C
IS-103 (comparison)	2.35	B	B	C
IS-104 (the invention)	2.42	A	A	A
IS-105 (the invention)	2.41	A	A	A
IS-106 (the invention)	2.42	A	A	A
IS-107 (the invention)	2.39	A	A	A
IS-108 (the invention)	2.39	A	A	A

[0179]

The results as above well support the effect of the invention.

[0180]

(Example 2)

Ultrapure water (resistance, at least 18 MΩ) was added to the components shown below to make one liter, and then stirred under heat at 30 to 40°C for 1 hour. Next, the resulting mixture was filtered under reduced

pressure through a micro-filter having a mean pore size of 0.25 μm . Inks of different colors were thus prepared.

[Formulation of Photo Cyan Ink]

(Solid Components)

Cyan Dye (C-1)	10 g/liter
Urea (UR)	15 g/liter
Benzotriazole (BTZ)	0.08 g/liter
Proxel XL2 (PXL)	3.5 g/liter

(Liquid Components)

Triethylene Glycol (TEG)	50 g/liter
Glycerin (GR)	100 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	60 g/liter
1,5-pentanediol (PTD)	40 g/liter
Isopropanol (IPA)	20 g/liter
Triethanolamine (TEA)	7 g/liter
Surfynol STG (SW)	10 g/liter

[0181]

[Formulation of Cyan Ink]

(Solid Components)

Cyan Dye (C-1)	30 g/liter
Urea (UR)	40 g/liter
Benzotriazole (BTZ)	0.08 g/liter
Proxel XL2 (PXL)	3.5 g/liter

(Liquid Components)

Triethylene Glycol (TEG)	40 g/liter
Glycerin (GR)	100 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	
	70 g/liter
1,5-Pentanediol (PTD)	50 g/liter
Isopropanol (IPA)	20 g/liter
Triethanolamine (TEA)	7 g/liter
Surfynol STG (SW)	10 g/liter

[0182]

(Formulation of Photo Magenta Ink)

(Solid Components)

Magenta Dye (M-1)	7.5 g/liter
Urea (UR)	10 g/liter
Proxel	5 g/liter

(Liquid Components)

Triethylene Glycol (TEG)	40 g/liter
Glycerin (GR)	100 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	
	60 g/liter
1,5-Pentanediol (PTD)	40 g/liter
Isopropanol (IPA)	20 g/liter
Triethanolamine (TEA)	6.9 g/liter
Surfynol STG (SW)	10 g/liter

[0183]

(Formulation of Magenta Ink)

(Solid Components)

Magenta Dye (M-1)	23 g/liter
Urea (UR)	15 g/liter
Proxel	5 g/liter

(Liquid Components)

Triethylene Glycol (TEG)	50 g/liter
Glycerin (GR)	100 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	50 g/liter
1,5-Pentanediol (PTD)	40 g/liter
Isopropanol (IPA)	20 g/liter
Triethanolamine	6.9 g/liter
Surfynol STG	10 g/liter

[0184]

(Formulation of Yellow Ink)

(Solid Components)

Yellow Dye (Y-1)	35 g/liter
Proxel	3.5 g/liter
Benzotriazole (BTZ)	0.08 g/liter
Urea	10 g/liter

(Liquid Components)

Triethylene Glycol (TEG)	40 g/liter
Glycerin (GR)	100 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	70 g/liter

1,5-Pentanediol (PTD)	60 g/liter
Isopropanol (IPA)	20 g/liter
Triethanolamine (TEA)	8 g/liter
Surfynol STG (SW)	10 g/liter
[0185]	
(Formulation of Black Ink)	
(Solid Components)	
Black Dye (BK-1)	75 g/liter
Black Dye (BK-2)	30 g/liter
Proxel	5 g/liter
Urea	10 g/liter
Benzotriazole	3 g/liter
(Liquid Components)	
Triethylene Glycol (TEG)	60 g/liter
Glycerin (GR)	100 g/liter
Triethylene Glycol Monobutyl Ether (TGB)	70 g/liter
1,5-Pentanediol (PTD)	50 g/liter
Isopropanol (IPA)	20 g/liter
Triethanolamine (TEA)	8 g/liter
Surfynol STG (SW)	10 g/liter
[0186]	

An ink set of these inks was prepared, and this is IS-201. In addition, other ink sets IS-202 to IS-208 were prepared in the same manner as above, to which,

however, the additive as in the following Table was added.
The dyes A to E used herein are all the same as those in
Example 1.

[0187]

[Table 3]

	Additive
IS-201 (comparison)	no
IS-202 (comparison)	A half of BK-1 in IS-101 was changed to dye A.
IS-203 (comparison)	A half of BK-1 in IS-101 was changed to dye B.
IS-204 (the invention)	A half of BK-1 in IS-101 was changed to dye C.
IS-205 (the invention)	A half of BK-1 in IS-101 was changed to dye D.
IS-206 (the invention)	1/3 of BK-1 in IS-101 was changed to dye C.
IS-207 (the invention)	1/3 of BK-1 in IS-101 was changed to dye D.
IS-208 (the invention)	A half of BK-1 in IS-101 was changed to dye E.

[0188]

These inks were charged in ink cartridges of CANON's inkjet printer PIXUS950i, and the printer was driven to print a stepwise density-varying image pattern of 6 colors C, M, Y, B, G and R and gray on an image-receiving sheet.

The image-receiving sheet used herein is copying woodfree paper, and Fuji Photo Film's inkjet paper, photo-glossy paper "Gasai".

The printed images were evaluated in the same manner as in Example 1.

The results are given below.

[0189]

[Table 4]

	Maximum Density	Light Fastness	Ozone Resistance	Ink Jet-Out Stability
PIXUS950i (comparison)	2.33	C	C	A
IS-201 (comparison)	2.11	A	A	C
IS-202 (comparison)	2.11	B	B	C
IS-203 (comparison)	2.15	B	B	C
IS-204 (the invention)	2.32	A	A	A
IS-205 (the invention)	2.31	A	A	A
IS-206 (the invention)	2.32	A	A	A
IS-207 (the invention)	2.33	A	A	A
IS-208 (the invention)	2.33	A	A	A

[0190]

The results as above well support the effect of the invention.

[Designation of Document] ABSTRACT

[Abstract]

[Task] To provide a black ink and ink set for inkjet which is high-density black images, and good image durability and ink jet out stability

[Means for Resolution] A black ink for inkjet, which comprises at least two dyes each having a value of λ_{max} within a range of from 500 nm to 700 nm, and having a half-value width of at least 100 nm in the absorption spectrum of the diluted solution thereof standardized to have an absorbance of 1.0, both dissolved or dispersed in an aqueous medium, and in which at least one dye has a positive oxidation potential over 1.0 V (vs SCE)

[Selected Drawing] None